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# JOURNAL

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# THE CHEMICAL SOCIETY

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
BRITISH AND FOREIGN JOURNALS.

## General and Physical Chemistry.

**Mean Intensity of Light that has passed through Absorbing Media.** By J. BOTTOMLEY (*Chem. News*, **44**, 212).

**Note on the Colour Relations of Nickel, Cobalt, and Copper.** By J. BOTTOMLEY (*Chem. News*, **44**, 212).—Some time ago the author described the preparation of a soluble black, and showed the advantages of such a solution in photometry; also its application to the determination of the law of absorption of light. Bayley recently gave the results of some similar investigations. He also finds that a mixture of nickel, cobalt, and copper is suitable. The following are the proportions of the metals in his and the author's solutions:—

	Ni.	Co.	Cu.
Bayley .....	1.48	1	2.16
Bottomley .....	1.49	1	2.46

D. B.

**Inversion of the Cyanogen Spectrum.** By G. D. LIVEING and J. DEWAR (*Ann. Chim. Phys.* [5], **23**, 571—573).—The authors have succeeded in obtaining photographs which show the inversion of lines in the spectrum of cyanogen between the violet and ultra-violet. The most complete inversion was obtained by employing the arc from a Siemens machine in a crucible of magnesia containing a considerable quantity of titanium cyanide. In this case, the photographs showed a complete inversion of five bands near L, two near N, and less complete of six bands commencing about wave-length 4215. No other metallic cyanide gives the same effect. Even a current of cyanogen passed into the crucible by a perforated carbon fails to yield a similar result. The only other nitrogen compound which affords a

result approaching that given by titanium cyanide is ammonium borate. The authors remark that there is no doubt that the great stability of titanium cyanide and nitrogen boride as compared with other nitrogen compounds, has a great influence on the result.

J. I. W.

**Spectrum Impressed on Silver Chloride, and its Bearing on Silver Printing in Photography.** By W. DE W. ABNEY (*Chem. News*, **44**, 184—185).—The place of maximum intensity at the least refrangible part of the spectrum impressed on silver chloride was observed to be at H, and when silver albuminate was used, the maximum effect was produced at G. In ordinary albuminised paper, both silver chloride and albuminate are present; in dull weather, the light is deficient in the ultra-violet rays: hence the larger proportion of work falls on the albuminate, and a lack of brilliancy in tone is the result. Care must therefore be taken in maintaining the right proportion of haloid to organic salts. The author suggests that the above facts may be made the basis of a scientific measurement of the radiation of total daylight.

J. K. C.

**Photochemistry of Silver Chloride.** By J. M. EDER and G. PIZZIGHELLI (*Wien. Akad. Ber.*, **82**, 144—160).—In this paper the following questions are investigated:—

1. How should silver chloride be prepared so as to be sensitive to light, and fit for chemical developers?
2. What are the general properties of the silver chloride undeveloped picture?
3. What are the best reagents for the development of this picture?

The authors point out that homogeneous silver chloride films can only be obtained by using an emulsion made from silver chloride and collodion or gelatin, &c. Silver chloride precipitated in presence of excess of a chloride is better than that precipitated in presence of excess of silver nitrate, on account of the tendency to irregular decomposition in the latter case. The sensitiveness of a pure silver chloride collodion emulsion is greatly increased, by the addition of such bodies as tannin, gallic acid, and morphine acetate, both as regards light and developers; the improvement is specially marked in the latter case. Silver chloride gelatin emulsions are much more sensitive than collodion emulsions. Digesting the emulsion only slightly increases the sensitiveness. The production of a latent picture is checked by the presence of alkaline chloride, and in a still higher degree by acids, such as hydrochloric and nitric. Ammonia greatly promotes the decomposition in light; ammoniacal silver nitrate can therefore be used to advantage for precipitating the chloride.

With regard to the second question, they show that the film changes as soon as it is exposed to light; it is blackened by a short exposure, owing to the formation of a subchloride insoluble in nitric acid; this is reduced to metallic silver by developers; by prolonged exposure, the plate becomes solarised. By treating a prepared plate with potassium bromide after exposure, the chlorine is replaced by bromine, and the plate becomes a silver bromide plate.

Several developers are mentioned; ammonio-ferrous-citrate in pre-

sence of free citric acid is recommended as the best, and is prepared as follows:—600 grams of citric acid are dissolved in 2 litres of water, and neutralised with ammonia; 400 grams of citric acid are now added, and the solution is diluted to 4 litres. 90 c.c. of this solution are mixed with 30 c.c. of a cold saturated solution of ferrous sulphate, and 6 c.c. of a sodium chloride solution (1:30). In all developers the addition of 0·1–0·3 per cent. of sodium chloride is very advantageous. Silver chloride plates require longer exposure than the bromide or iodide plates. The time depends on the developer, being less when the developer is concentrated, or when its action is very energetic. The reduced silver formed on treating an exposed plate with developers, when seen by transmitted light in thin films, appears of different colours, according to the method employed, *e.g.*, that from ordinary silver chloride is yellow-red to red-brown, whilst that from silver chloride which has been digested for some time, or that prepared from ammoniacal silver nitrate, is dark-brown, black-violet to black. When developed with ammonio-ferrous-citrate, the silver from the former is red-brown, from the latter black-brown. With other developers yellow-brown or red, or red-brown silvers are obtained. Silver chloride gelatin is sufficiently sensitive to produce by direct gaslight in 20–30 minutes a completely finished positive from a photographic negative.

Silver chloride is preferable to the more sensitive bromide for the production of more modified pictures, because the development can be better controlled.

The best reagent for fixing silver chloride plates is sodium thiosulphate.

D. A. L.

**Radiant Matter from Electrodes.** By J. PULUJ (*Chem. Centr.*, 1881, 193–194).—As a further proof of the author's view that so-called radiant matter consists of particles detached from the electrodes, an experiment is described with cathodes covered with chalk. The cathodes shone with an orange phosphorescent light, and the walls of the glass vessel in a short time became covered with an exceedingly fine layer of chalk, and showed, in spite of their apparently complete purity and transparency, a phosphorescence like that of the chalk. The yellow stratum which first appears on metallic cathodes is a phosphorescent phenomenon, due to a thin film of metallic oxide. The paper concludes with a detailed criticism of Goldstein's investigations on radiant matter.

T. C.

**Thermal and Volumetric Researches on Formic and Acetic Acids.** By O. PETTERSSON (*J. pr. Chem.* [2], 24, 293–310).—The melting points of these two acids do not appear to have been correctly ascertained, but it is believed that the figures here given are correct. Pure formic acid melts at + 7·45°, and pure acetic acid at + 16·55°. Rüdorff, by repeated crystallisation purified acetic acid, so that it melted at 16·70°. The latent heat of formic acid, when passing from the solid to the liquid state, is found to be 57·38, so that when the molecule  $\text{H.COOH}$  solidifies, 2639 units of heat are disengaged, but as the specific heat of the solid acid is unknown, the true latent heat



$C_2H_4O_2$  (Vapour-density = 2.08).

	Temperature.	Density.
$C_2H_4O_2$ .....	157.5°	2.747
„ .....	161.1	2.620
„ .....	214.0	2.229
$C_2H_4O_2$ + 1.13 p. c. aq. ....	161.0	2.527
„ .....	214.0	2.140
$C_2H_4O_2$ + 1.915 p. c. aq. ....	160.8	2.501
$C_2H_4O_2$ + 8.414 p. c. aq. ....	160.5	2.298
„ „ „ .....	214.0	2.122

These figures show clearly that with a rise of temperature a gradual dissociation occurs. The specific heat of formic acid is but little affected by water, but that of acetic acid is considerably, varying from 0.479 when pure, to 0.513 when the mixture is 100 Ac + 8.414 per cent. aq., and between 0° and 47°.

If instead of reckoning the results from the unit of weight, the calculations are made from the respective molecular weights of the acids, it is found that in their physical properties they are almost identical.

	Latent heat of fusion.	Contraction when solid.	Coefficient of expansion.
$CH_3CO_2$ .....	2694	12.33 p. c.	0.001028
$C_2H_3O_4$ .....	2657	12.58 „	0.001052

In the case of the coefficient of expansion “corresponding” temperatures are employed, that is, temperatures close to the melting points of each acid, and then the expansions are proportional.

E. W. P.

**On Drops Floating on the Surface of Water.** By O. REYNOLDS (*Chem. News*, 44, 211).—The results of a number of experiments point to the conclusion that whatever may be the cause of this suspension, it depends on the surface of the water being pure and free from scum, and not at all on the temperature or condition of the air.

D. B.

**Studies in Chemical Processes.** By F. WALD (*Monatsh. Chem.*, 1881, 171—191).—A very large number of chemical processes, developing much energy, can occur only under the influence of exterior causes, heat, light, &c. The author considers that the theory previously offered to account for this is insufficient, and suggests the following hypothesis:—“*That for the completion of a chemical reaction developing much energy, it is necessary that a portion of this energy be withdrawn from the molecules then at the point of formation, and this applies to all cases in which the energy developed is sufficient to heat the new molecules above the temperature at which they are still stable.*” This withdrawal of energy he holds to be effected by other molecules present, which for the moment take no further part in the reaction. It is usually assumed that only those molecules react which, in the course of their paths, come into actual impact, and as, especially in the case of gases, the dimensions of the molecules are very small in com-

parison with their mean distance, the probabilities are very great against more than 2 or 3 mols. being in contact at one time under normal conditions. To take as an instance, the union of hydrogen and oxygen, the equation  $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$  requires the contact of only 3 mols., but the amount of heat generated (136,720 heat-units) is so much in excess of that required to bring the newly-formed molecules to the superior limit of dissociation (say  $3,000^\circ$ ) that it would further suffice to heat 5.3 mols. of gas to that temperature; so that instead of only 3 mols. the co-operation of 8 to 9 mols. is requisite for the completion of the reaction: the contact of such a number of molecules in a gaseous mass could scarcely be assumed without some special exciting cause. Consideration of a number of analogous cases leads to a similar result, and it is especially shown that of two comparable reactions, that one which develops least energy will occur with the greatest readiness.

With regard to the manner in which the necessary number of atoms can be brought into contact, this can be effected in many cases by raising the temperature; the velocity of the molecules increases proportionally to the square root of the absolute temperature, whilst the mean molecular distance, especially with liquids and solids, increases much more slowly: the number of impacts of molecules therefore rises with the temperature. In many cases, where this is still insufficient, the assumption may be made of a sudden difference of temperature in adjacent layers; the heated molecules, by their flying apart, compress the molecules together in the cooler layers, and so cause the necessary impacts. That many of these reactions can be effected by pressure, percussion, friction, or sound waves of short wave-length, is also in agreement with the theory, all these causes tending to produce contact of some number of molecules.

The author then refers to the relative sizes of the flames of various gases when burnt under similar conditions, and shows that they vary as the *total* number of molecules required according to his theory. Luminous flames he attributes to a deficiency of molecules available for cooling, so that only processes developing but little energy can occur in the inner parts of the flame; on dilution with another gas, the luminosity ceases. Wibbel has shown that if the diluting gas be oxygen, the amount employed must be more than is requisite for the combustion of the luminous particles, and the author finds that the luminosity of a small flame can be removed by inserting a suitably shaped platinum wire into it, the luminosity returning when the wire has become heated to glowing.

A reaction very often becomes possible when a bye-process occurs which consumes a portion of the surplus energy; and in the case of gases reactions are sometimes rendered possible by bringing them into solution, for in liquids the mean molecular distance is less, and the necessary number of molecules more readily brought together.

A. J. G.

**New Method of Measuring Chemical Affinities.** By A. TRIBE (*Chem. News*, **44**, 185).—On the supposition that if in a series of trials the chemical affinities were altered while the other circumstances remained the same, the magnitude of the intermedial space

between the boundaries of the electro-deposits on metallic plates, immersed in an electrolytic field, would increase along with the force required to overcome the affinities of the ions of the electrolyte, a series of experiments were made with molecular solutions of zinc chloride, bromide, and iodide, with plates of Ag, Cu, Fe, and Zn, and the anticipated results were obtained; the intermedial space with the chloride was greatest, the bromide less, and the iodide least. Another series with silver plates and molecular solutions of zinc and copper sulphates, showed that the intermedial space in the case of zinc sulphate was much the greater. Experiments with zinc, iron, copper, and silver, showed that here again the spaces followed the order of the respective chemical affinities.

J. K. C.

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## Inorganic Chemistry.

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**The Halogens.** By H. ZÜBLIN (*Annalen*, 209, 277—308).—After giving a historical sketch of our knowledge of chlorine, with special attention to the murium oxide theory, lately revived by Victor Meyer's experiments, the author proceeds to describe experiments he has made, with the view of definitely settling the question whether oxygen can be obtained from pure chlorine. Porcelain tubes made at Bayeux, and glazed on the outside only, were first used; pure and dry chlorine was passed through at a yellow heat, and in all cases small quantities of oxygen were detected in the issuing gas; that this could not have its origin in moisture contained in the chlorine was ensured by passing it through four long tubes containing phosphoric anhydride, previous to entering the porcelain tube. An attempt was then made to separate the oxygen by diffusion through a platinum diaphragm, pricked with fine holes, and placed in a Berlin porcelain tube, the unalterability of Berlin porcelain and platinum, when in contact with chlorine at a yellow heat, being first ascertained by experiment. No oxygen at all could be traced by means of diffusion, and the only explanation remaining was that the oxygen obtained in former experiments arose from the Bayeux porcelain employed. That this was its true source was placed beyond doubt from the fact that chlorine passed through a platinum tube surrounded by Berlin porcelain, gave up no oxygen at all at a yellow heat, but when the platinum tube was filled with fragments of Bayeux porcelain, small quantities of oxygen were easily traced. No oxygen being therefore obtained from chlorine, the behaviour of iodine at a bright yellow heat was next studied. The vapour of iodine in a strongly heated Berlin porcelain tube, was allowed to diffuse into carbonic anhydride, without the smallest quantity of oxygen being traced in the latter; here again negative results were obtained.

The vapour-density of chlorine, which had been exposed to a yellow heat, was found on cooling to 100° to be normal. It appeared of interest to repeat the experiments of Davy and Gay-Lussac with

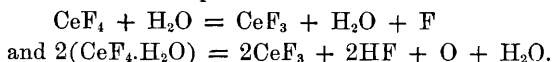


reference to the behaviour of chlorine at a strong heat in contact with charcoal, extending the experiments also to bromine or iodine. In the first instance, Berlin porcelain tubes were used, and when the temperature approached a yellow heat, a gas was found to issue along with the chlorine, not absorbed by potash, and which on further examination proved to be carbonic oxide; on observing the charcoal at the end of the experiment, it was found that the porcelain had been attacked, but no carbonic oxide or any other gas not absorbed by potash was formed when chlorine or bromine was passed over charcoal in a platinum tube, at the strongest heat of a Schlösing's furnace.

In the course of the foregoing experiments a piece of perforated platinum foil was made, which was found to be impervious to chlorine, although it allowed air to pass through freely. J. K. C.

**Formation of Free Fluorine.** By B. BRAUNER (*Ber.*, **14**, 1944—1946).—On heating cerium tetrafluoride,  $\text{CeF}_4 + \text{H}_2\text{O}$ , or its double salt,  $3\text{KF} + 2\text{CeF}_4 + 2\text{H}_2\text{O}$ , a lower fluoride is formed, and a gas is evolved (probably free fluorine) which resembles chlorine or hypochlorous acid in odour.

The reactions which take place are—



The anhydrous lead tetrafluoride is also decomposed by heat, with formation of the difluoride and a gas which has a strong odour of chlorine. W. C. W.

**Iodammonium Iodide.** By W. H. SEAMON (*Chem. News*, **44**, 188—189).—Perfectly dry ammonia gas was passed over iodine in a flask surrounded by ice; the product was allowed to remain at rest in a weighed bottle over sulphuric acid, in a desiccator surrounded by ice, until of constant weight; it was then analysed, and was found to be identical with the compound  $\text{NH}_3\text{I}_2$ , prepared by Guthrie.

J. K. C.

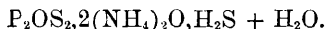
**Quantivalence of Phosphorus.** By H. GOLDSCHMIDT (*Chem. Centr.*, 1881, 489—495).—The question as to whether phosphorus is always trivalent, or sometimes pentavalent, is discussed by the author at some length. After glancing at those compounds built up on the ammonium type, he considers the arguments against and in favour of the occasional pentavalency of phosphorus in such compounds as the oxychloride and pentachloride. The formula of the former on the assumption of the trivalency of phosphorus, may be represented as  $\text{Cl}_2\text{P}-\text{O}-\text{Cl}$ , in which 2 atoms of chlorine are directly united to phosphorus, and 1 indirectly through the medium of an atom of oxygen. The author considers that the question as to the atomic volume of oxygen in this body is at present unsettled, in view of the results of Thorpe and Ramsay, and he has proceeded to investigate the constitution of phosphorus oxychloride from a different stand-point. It appears strange that the above graphic formula should be correct, when we consider that the oxychloride is a very stable body, and that other

compounds which contain chlorine in direct combination with oxygen, are very easily decomposed, such as the oxides of chlorine and hypochlorites, and the so-called chlorine acetate. According to the above formula also, 1 atom of chlorine having a different situation in the molecule to the other two, ought to behave differently in reactions with other bodies. In order to test the correctness of this statement, reactions with various metals and elementary substances, namely, Ag, Cu, Hg, Fe, Sn, As, P, Zn, Mg, and Al, were studied. The reactions began mostly at 200–250°, zinc alone showing any action in the cold. No difference in the affinity of the chlorine-atoms for phosphorus was observed, the general reaction being that the oxygen was first abstracted by the metal, with formation of trichloride, which again came into operation, making the final product a complicated one, consisting of phosphates, pyrophosphates, and chlorides of the metal, together with  $\text{PCl}_3$ ,  $\text{P}_2\text{O}_6$ ,  $\text{P}_2\text{O}_3\text{Cl}_4$ , and  $\text{P}_4\text{O}$ , some of these being present and some absent in various cases, and phosphorus trichloride being always formed, except in the presence of zinc and copper, which remove all three chlorine-atoms, leaving the group PO. These reactions, therefore, point to  $\text{Cl}_3\text{P} : \text{O}$  as being the correct formula for the oxychloride, in which phosphorus is a pentad. Taking the case of the pentachloride, the theory that this body is a molecular compound formed from the two groups  $\text{PCl}_3$  and  $\text{Cl}_2$ , is rendered improbable by the existence of the pentafluoride, in which phosphorus can only be regarded as a pentad. In its reactions with metals and metalloids, the pentachloride behaves in a manner analogous to that of the oxychloride, in that two chlorine-atoms are as easily abstracted from the former as the oxygen from the latter. The author also argues that, supposing  $\text{PCl}_5$  to be a molecular additive compound of  $\text{PCl}_3$  and  $\text{Cl}_2$ , two chlorine-atoms must be bound together as in free chlorine,  $\text{Cl}-\text{Cl}$ , and the action of the pentachloride, as far as these two atoms of chlorine are concerned, should be the same as that of free chlorine. If, however, phosphorus pentachloride is found to chlorinate a body under conditions where free chlorine is inactive, then the two atoms of chlorine must be linked together by a weaker affinity in the pentachloride than they are in chlorine, and therefore the molecule  $\text{Cl}_2$  cannot exist, as such, in  $\text{PCl}_5$ . This was in fact found to be the case; platinum at 250° is converted into dichloride by phosphorus pentachloride, but remains unaltered in a stream of chlorine; or, when heated with chlorine, in a sealed tube. The author considers, therefore, that the most rational explanation which can be given is to acknowledge the varying quantivalence of phosphorus from the triad to the pentad condition.

J. K. C.

**Sulphur Salts derived from Phosphorus Trisulphide.** By G. LEMOINE (*Compt. rend.*, 93, 489–492).—Phosphorus trisulphide is rapidly decomposed by a solution of soda with evolution of hydrogen mixed with hydrogen phosphide, and separation of a small quantity of free phosphorus. When this solution is evaporated in a vacuum, it yields crystals of the composition  $\text{P}_2\text{OS}_2 \cdot 2\text{Na}_2\text{O} + 6\text{H}_2\text{O}$ . When the phosphorus sulphide acts on sodium sulphhydrate, hydrogen sulphide and phosphide are evolved, and the

solution, on evaporation in a vacuum, yields crystals of the composition  $\text{P}_2\text{OS}_2, 2\text{Na}_2\text{O}, 2\text{H}_2\text{S} + 4\text{H}_2\text{O}$ . The solution obtained by the action of the sulphide on ammonium sulphhydrate, deposits crystals of the composition  $\text{P}_2\text{OS}_2, 2(\text{NH}_4)_2\text{O}, 3\text{H}_2\text{S}$ , which, when dried at  $100^\circ$  in a current of hydrogen sulphide, yield the compound



The mother-liquor, when evaporated in a vacuum, deposits crystals of the composition  $\text{P}_2\text{OS}_2, 2(\text{NH}_4)_2\text{O} + 2\text{H}_2\text{O}$ .

All these salts are of the same type. They all contain 2 atoms of sulphur replacing 2 atoms of oxygen in phosphorous acid, and in some of them the water of crystallisation, and even the water of constitution of the phosphorous acid, has been replaced by hydrogen sulphide. In the latter case, the salts lose hydrogen sulphide at ordinary temperatures. All the compounds give precipitates with most of the metallic salts. With lead acetate, they give a precipitate of the corresponding lead compound, which may contain either  $2\text{PbO}$  or  $3\text{PbO}$ , and has a colour varying from yellow to red. It soon decomposes into lead sulphide and phosphorous acid. With hydrochloric acid the solid compounds give off hydrogen sulphide. When heated to  $200$ – $240^\circ$ , they lose hydrogen sulphide but retain a portion of their sulphur, even after prolonged ignition. When their aqueous solutions are boiled, all the sulphur is given off as hydrogen sulphide, an alkaline phosphite being formed. The existence of these compounds affords further proof of the analogy between oxygen and sulphur.

C. H. B.

**Preparation of Sulphuryl Chloride, a Contribution to our Knowledge of Catalysis.** By H. SCHULZE (*J. pr. Chem.* [2], **24**, 168–183).—The author enumerates and considers the various bodies which help to effect the formation of sulphuryl chloride from sulphurous anhydride and chlorine gases without the help of sunshine, viz., ethylene, charcoal, glacial acetic acid, and camphor, of which latter he has already given some account. The absorption of sulphurous anhydride by camphor, which thereby becomes liquefied, was first studied by Bineau, and in agreement with his determinations the author found that at 725 mm. and  $0^\circ$  the camphor had condensed 0.880 of its weight of the gas; on exposure to the air all the absorbed gas rapidly escapes. Chlorine has no action on camphor, but it is greedily absorbed by the above liquid until saturated, and a solution of camphor in sulphuryl chloride is formed, which can be easily separated and obtained pure by distillation. This action cannot be due to the mere condensation of the sulphurous anhydride and its action in the liquid state on the chlorine, for these two gases do not combine even when condensed and cooled to  $-20^\circ$ ; but, on the other hand, in presence of camphor the reaction takes place even at  $-20^\circ$ . Sulphurous anhydride combines in large proportion with and liquefies glacial acetic and formic acids; these acids are scarcely attacked by chlorine if sunlight is excluded, but the sulphurous compounds greedily absorb chlorine with formation of sulphuryl chloride, the acetic and formic acids remaining almost unacted on; thus their mode of action seems to resemble that of camphor. Alcohol and acetone also absorb quanti-

ties of sulphurous anhydride; chlorine passed through these liquids acts on the alcohol and acetone, and in proportion as this proceeds the sulphurous anhydride escapes without being acted on. Other absorbents of sulphurous anhydride are sulphuryl chloride itself, and liquid sulphuric anhydride. Chlorine passed into the latter solution does not yield a trace of sulphuryl chloride, no more than it does with the former. In this case, a few bubbles of chlorine passed into the solution were sufficient to produce a yellow coloration, thus showing the chlorine to be simply dissolved, and after a time the chlorine passed through unaltered; the point is also proved by the fact that no appreciable increase of weight took place when chlorine was passed into sulphuryl chloride previously saturated with sulphurous anhydride (it absorbed 32.4 per cent).

Turpentine absorbs sulphurous anhydride, but it does not effect the union of this body with chlorine. Carbon bisulphide and chloroform absorb chlorine, but the solution is not acted on by sulphurous anhydride.

It cannot be supposed that the action of camphor, or acetic or formic acids, is due to their combining momentarily with chlorine, and then passing it over to the sulphurous anhydride *in statu nascendi*, for the first two undergo substitution to a slight extent only, and the last is completely decomposed into carbonic anhydride and hydrochloric acid.

If chlorine is passed into a solution of sulphurous anhydride in camphor, but not to saturation, and the bulk of the sulphuryl chloride is then removed by distillation and the rest by shaking repeatedly with water, there remains pure camphor containing no trace of chlorine substitution-products. But, if chlorine is passed to saturation, substitution-products are formed, and increase in quantity on standing and introduction of more chlorine; at 0°, however, this action is extremely slow.

By passing sulphurous anhydride and chlorine gases alternately through a flask containing a small quantity of camphor (5 grams), a large quantity of sulphuryl chloride can be easily prepared (*viz.*, 47.2 grams after fifteen operations, when the action had almost ceased). The solvent power of the sulphuryl chloride formed doubtless helps the action of the camphor; but this dilution of the camphor, most favourable at 1 : 50, stops the reaction at 1 : 100. A mixture of the two gases has naturally the same effect as above, but not until about two parts of sulphuryl chloride are formed to one of camphor does the reaction go on rapidly. With glacial acetic acid, the preparation may be carried on just as easily, but with formic acid, when about five times its volume of sulphuryl chloride is formed, the liquid separates into two layers, the upper one consisting of the formic acid containing some sulphuryl chloride.

If bromine or iodine is added to the solution of the camphor in sulphurous anhydride, substitution-products alone are formed, and no sulphuryl bromide or iodide. Neither were these bodies obtained by the action of sulphuryl chloride on hydrobromic or hydriodic acids or their salts; all are decomposed even at the ordinary temperature, with separation of sulphurous anhydride and bromine or iodine, thus:

$$2\text{HI} + \text{SO}_2\text{Cl}_2 = 2\text{I} + \text{SO}_2 + 2\text{HCl}.$$

H. B.

**Hydration of Salts and Oxides.** By C. F. CROSS (*Chem. News*, **44**, 209).—By subjecting the method of investigating the difficult problem of rehydration to a critical examination, the following of the more important facts were established. The author used the apparatus previously described by him (*Chem. News*, **44**, 101). Copper sulphate combines with decreasing velocity with  $5\text{H}_2\text{O}$ , at which point it remains constant for some time; it then proceeds to take up additional water, although with much less velocity, and in fact deliquesces; this is important, as showing that from hydration to solution there is an actual and unbroken series of combinations. Sodium sulphate, potassium sulphate, and magnesium sulphate pass through hydration to deliquescence without break; potassium dichromate gives a third type of hydration, inasmuch as at the ordinary temperature of the air and exposed under a bell-jar to an atmosphere saturated with aqueous vapour it “condenses” water to the molecular limit of  $3.5\text{H}_2\text{O}$ , none of which water can be said to be combined with the salt, as it is entirely removed by pressure between blotting paper. Precipitated ferric oxide, dried at  $100^\circ$ , and containing 1 mol.  $\text{H}_2\text{O}$ , hydrates rapidly at first, but after taking up 1 mol. water, the combination proceeds very slowly. D. B.

**Crystals Produced by the Action of Metals Sealed up in Carbon Bisulphide.** By P. BRAHAM (*Chem. News*, **44**, 211).—Fifteen different metals were sealed up in carbon bisulphide on June 20th, 1879. On June 20th, 1880, the tubes were examined under the microscope, when appearances of incipient crystallisation were observed; and on May 20th, 1881, transparent crystals were found in those tubes, which contained gold, antimony, and bismuth. The experiment is being continued. D. B.

**Conversion of Sodium Sulphate into Hydroxide.** By C. F. CROSS and E. J. BEVAN (*Dingl. polyt. J.*, **242**, 137).—The object of this investigation is to replace the conflicting and uncertain data touching the reaction  $\text{Na}_2\text{SO}_4 + \text{Ca}(\text{OH})_2 = \text{CaSO}_4 + 2\text{NaOH}$  by more exact and trustworthy numbers than those which at present exist. The chief factors of the limit of the decomposition are the partial solubilities of the calcium compounds. Calcium hydroxide was found to be practically insoluble in a 2–3 per cent. solution of sodium hydroxide. Calcium sulphate was found, as stated by Poggiale, to have a maximum solubility at  $35^\circ$ , and at this temperature the decomposition was 10 per cent. lower than at  $15^\circ$ , all other conditions being equal. In all experiments upon the conversion in question, the authors employed 5 grams  $\text{Na}_2\text{SO}_4$  and 2 grams  $\text{CaO}$ , quantities which are in the ratio of the molecular weights. In aqueous solution, both at the ordinary and at the boiling temperature, the maximum decomposition was reached with a volume of 350 c.c., when, *i.e.*,  $\text{NaSO}_4 : \text{H}_2\text{O} = 1 : 550$ . The limits were, in the first case (duration 7 days) 35 per cent. of the salt employed; in the latter (duration 4 hours) 11.4 per cent. The influence of time will be seen from the following table:—

Duration of experiment.	At 15° C. Yield per cent.	At 100°. Yield per cent.
4 hours	12·9	10·42
20 "	—	10·8
35 "	—	19·6
40 "	23·5	—
96 "	—	25·2
7 days	{ (1.) 28·0 } { (2.) 28·7 }	25·3
14 "	28·8	—

The condition of rest or motion of the liquid was found in four comparative experiments, in which the duration was one week, to be without sensible influence.

By addition of alcohol, 23 per cent. by volume, the yield of alkali (at 15°) was increased to 55 per cent. of the theoretical. This was the maximum attained, and represents the most favourable adjustment of the solubilities both of reagents and of products. The yield of alkali was found to be increased by the addition of sugar (5 grams) to the boiling aqueous solution, from 11·4 to 20 per cent.; on the other hand, by the addition of sodium chloride (5 grams) to be decreased from 11·4 to 7·1, the first-named influencing the solubility of the calcium hydroxide, the latter that of the sulphate. The authors also investigated the limit of occurrence of the inverse decomposition, and found that this appears to commence when the alkaline strength reaches 0·3 per cent. ( $\text{Na}_2\text{O}$ ); this strength did not obtain in any of the experiments upon the first-named reaction.

The results of the determinations, which are very numerous, are comprised in tables for which the original must be consulted.

C. F. C.

**Hydrated Barium Nitrate.** By R. A. BERRY (*Chem. News*, **44**, 190).—By saturating the same water with barium and strontium nitrates, introducing a crystal of  $\text{Sr}(\text{NO}_3)_2 + 4\text{H}_2\text{O}$ , and evaporating in a vacuum over sulphuric acid, crystals were obtained containing 17 per cent. of a hydrated barium nitrate, isomorphous with the strontium compound.

J. K. C.

**Magnesium Carbonates.** By H. BECKURTS (*Arch. Pharm.* [3], **18**, 429—442, and [3], **19**, 13—23).—Pattinson (*Chem. News*, 1863, 128) described a process for preparing *Magnesia alba*, consisting in treating slightly ignited dolomite with carbonic anhydride and water under 5—6 atmospheres' pressure, when it is found that so long as any magnesium carbonate remains undissolved, so long will the calcium carbonate remain unacted on, the solution in the carbonic anhydride and water being of acid magnesium carbonate only. When this solution is heated with steam, *magnesia alba* is precipitated as a bulky powder. The author confirms the statement that unignited dolomite yields no solution of magnesium carbonate when treated with carbonic anhydride under pressure, from which he concludes that in dolomite we have a double carbonate of calcium and magnesium, which, on igniting, splits up partially into carbonic anhydride, and into the separated carbonates of the bases.

The purity of the carbonic anhydride, in addition to that of the dolomite and the water, is not without influence on the product. At the Nauheim factory a very pure gas, which escapes from the ground in the neighbourhood, is employed.

On triturating *magnesia alba* with water and passing carbonic anhydride through the liquid, a solution is obtained which, on spontaneous evaporation, yields a neutral magnesium carbonate with 3 mols. of water of crystallisation, of sp. gr. 1.875. The author finds that 658 parts of water at 19° dissolve 1 part of this salt. Neutral magnesium carbonate is also obtained by the double decomposition of a soluble magnesium salt with sodium carbonate.

The author found the ratio of magnesium oxide to carbonic anhydride in solutions of magnesium carbonate in water containing this gas, to be approximately 1 : 2 (in equivalents), whence he concludes that such solutions contain the salt  $\text{Mg}(\text{HCO}_3)_2$ .

On heating a litre of a 3.71 per cent. magnesium carbonate solution for about five minutes at 70–75°, an abundant evolution of carbonic anhydride occurs, and crystals of neutral magnesium carbonate separate. The filtrate containing 1.2 per cent. of magnesium carbonate, heated to 71° for five minutes, again evolves gas, but deposits an appreciably smaller amount of neutral carbonate. On boiling the filtrate from this, a few decigrams of a basic carbonate were deposited containing 42.7 per cent. of magnesium oxide. The author further found, on boiling a solution of magnesium carbonate in carbonic anhydride, that he always obtained the same basic salt, the concentration of the solution and the duration of the boiling, having no influence on its composition. From analysis of this basic body, and the composition of *magnesia alba* from various sources, the author deduces for *magnesia alba* the formula  $5\text{MgCO}_3 \cdot 2\text{Mg}(\text{OH})_2 + 7\text{H}_2\text{O}$ , which requires 42.4 MgO, 34.2  $\text{CO}_2$ , and 22.4  $\text{H}_2\text{O}$ .

H. Rose (*Ann. Chem. Pharm.* **80**, 231) investigated more minutely the precipitates produced by alkaline carbonates with magnesium salts, and deduced the formulæ:  $4\text{MgCO}_3 + \text{Mg}(\text{OH})_2 + 4\text{H}_2\text{O}$ ,  $4\text{MgCO}_3 + \text{Mg}(\text{OH})_2 + 5\text{H}_2\text{O}$ ,  $3\text{MgCO}_3 + \text{Mg}(\text{OH})_2 + 5\text{H}_2\text{O}$ , and  $3\text{MgCO}_3 + \text{Mg}(\text{OH})_2 + 4\text{H}_2\text{O}$ . The author also in two cases found commercial products of the composition of the last formula. On boiling the neutral air-dried carbonate with much water, a salt,  $3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 + 5\text{H}_2\text{O}$ , as above was obtained. Kraut (*Arch. Pharm.*, **217**, 252) has published analyses of magnesium products more or less agreeing with those of the author.

The *magnesia carbonica ponderosa* of the Pharmacopœia is obtained by double decomposition of magnesium sulphate and sodium carbonate, evaporation of the mixture, washing with hot water, and drying at 100°. Its composition is  $3\text{MgCO}_3 \cdot \text{MgO} + 5\text{H}_2\text{O}$ . Corresponding to the two varieties of *magnesia carbonica* of the British Pharmacopœia are a heavy and light *magnesia usta*. The sp. gr. of *magnesia usta levis* (obtained from light *magnesia alba*) is 2.74; the sp. gr. of *magnesia usta* (from *magnesia carbonica ponderosa*) is 3.057; that of *magnesia usta* (obtained by ignition of neutral magnesium carbonate) 3.69. With reference to the presence of calcium carbonate in magnesium preparations, the author remarks that a less quantity than 3 per cent.

cannot be detected by ammonium carbonate. Oxalic acid does not give appreciably better results. By Biltz's method,  $\frac{1}{2}$  per cent. of lime can be detected, but by the Graham-Otto method (Graham-Otto, *Lehrb.*, 4th Edit., 2, 614), by igniting and extraction with water, the author has succeeded in detecting 0.01 per cent. of calcium carbonate in *magnesia alba*.  
F. L. T.

**Sulphochromites.** By M. GRAEGER (*Monatsh. Chem.*, 2, 266—275).—The author has already prepared the sulphochromites of zinc, iron, and manganese,  $M'Cr_2S_4$ , by heating a mixture of the hydroxides of chromium and zinc, &c., with sulphur. These compounds are dark brown or black powders, insoluble in water and in hydrochloric acid, but soluble in nitric acid and in aqua regia (Abstr., 1881, 225). The present paper describes the preparation and properties of several other sulphochromites.

*Sodium Sulphochromite* or *Sodiochromic Sulphide*,  $Na_2Cr_2S_4$ , is prepared, like the zinc salt, by triturating 1 gram of chromic hydroxide dried at a comparatively low temperature with 9 g. anhydrous sodium carbonate and 11 sulphur to a fine homogeneous powder; heating the mixture in a covered porcelain crucible, filled to about three-fifths, till the sulphur begins to volatilise and burn at the edge of the crucible; and keeping up the heat for about a quarter of an hour longer, but discontinuing it before the whole of the sulphur is volatilised, so that the crucible may be still full of sulphur-vapour, and the oxygen of the air be thereby prevented from coming in contact with the mass while it is still hot.

The melt, after cooling, is drenched with a quantity of water sufficient to take up all the soluble sulphide of sodium; the undissolved portion is washed by decantation with a solution of 15 g. caustic soda in a litre of water, till neither sulphide nor thiosulphate can be detected in the decanted liquid; the soda is washed away with strong spirit (90 per cent. Tr.), which is in its turn displaced by absolute alcohol; and the precipitate is drained on a filter and quickly dried.

The salt thus obtained is a dark brick-red amorphous powder, which in the dry state is not altered by contact with the air at ordinary temperatures, but glows when heated, giving off sulphurous anhydride, and leaving a mixture of chromic oxide and sodium sulphate, the decomposition taking place according to the equation,  $Na_2Cr_2S_4 + O_{18} = Na_2SO_4 + Cr_2O_3 + 3SO_2$ .

Sodiochromic sulphide is insoluble in water, but when triturated therewith it is brought into a state of extremely minute division, so that it passes through the thickest filters, beginning to blacken at the same time. This change of colour is due to oxidation, and takes place even in water which has been de-aërated as completely as possible by boiling; but if the water be perfectly deoxygenised by mixing it, after boiling, with solution of ferrous sulphate and potash-ley, and leaving the whole for some time in an atmosphere of pure hydrogen, and this deoxygenated water be then distilled over into a receiver containing the sodium salt, which is likewise traversed by a stream of hydrogen and then closed air-tight, the salt will remain for months



without exhibiting the slightest change of colour. If the pulverised sodium sulphochromite is suspended in a solution of caustic soda of the strength above mentioned, it sinks down pretty quickly, and will remain quite unaltered in colour for weeks, even if a stream of air be passed through the liquid. From this it would appear that the oxidation of the salt by the action of the air takes place only when it is in a very finely divided state, and that the soda, by causing it to aggregate in larger particles—as is evident from the fact of its sinking rapidly in that liquid—prevents the oxidation. A similar behaviour is exhibited by iron pyrites, which in the moist state is oxidised by the air only when it is in a state of minute division, so that a clay-slate containing particles of iron pyrites large enough to be seen with the naked eye, is not well adapted for the preparation of alum or of ferrous sulphate.

Sodiochromic sulphide is not attacked by strong hydrochloric acid, and but slightly when heated with dilute hydrochloric or sulphuric acid; by strong nitric acid and aqua regia on the other hand, it is readily dissolved at ordinary temperatures, and by dilute nitric acid, when heated, with formation of the sulphates of chromium and sodium. Strong sulphuric acid scarcely attacks it in the cold, but on raising the temperature, blackening takes place, sulphurous anhydride is evolved, and sulphur separated, and the compound dissolves completely, forming a green solution containing the sulphates of sodium and chromium.

All attempts to prepare the corresponding sulphides of chromium and *potassium* were unsuccessful. On treating chromic hydroxide with potassium carbonate and sulphur as above described, using these substances even in much larger excess than in the preparation of the sodium salt, a black melt was obtained, from which water dissolved out polysulphides and thiosulphate of potassium, leaving a black crystalline mass, which was found by analysis to be nothing but chromic sulphide. The formation of a potassio-chromic sulphide was however observed by Schafarik (*Wien. Akad. Ber.*, **47** [2], 253), on fusing potassium chromate with liver of sulphur.

The sulphochromites of the heavy metals are obtained by precipitating the sodium-salt with various metallic solutions. The *iron*, *manganese*, and *zinc salts*, thus prepared exhibit, with exception of a darker colour, the same properties as those formerly obtained by the author in the dry way (Abstr., 1881, 226). The other sulphochromites are all black or greenish-black pulverulent bodies, insoluble in water. They are not attacked by hydrochloric acid, but dissolve readily, with oxidation, in nitric acid, forming the corresponding metallic salts. The *tin salt* thus treated leaves metastannic acid; the *lead salt*, lead sulphate. They are all likewise soluble in aqua regia, the *silver salt* of course yielding a precipitate of silver chloride.

The sulphochromites, when heated in the air, burn away with a glimmering light, and evolution of sulphurous anhydride, the silver, copper, cadmium, cobalt, nickel, and manganese salts, leaving residues consisting of chromic oxide and the corresponding sulphates, the iron and tin salts leaving chromic oxide mixed with ferric and stannic oxide respectively, and the lead and zinc salts leaving the corresponding chromites. These

reactions serve as the basis for the quantitative analysis of the sulphochromites.

The sulphochromites of barium, strontium, and calcium cannot be prepared from the sodium salt by double decomposition, inasmuch as the reaction is very slow and incomplete, and during its progress the sodium salt becomes oxidised and decomposed in the manner already mentioned.

The existence of the sulphochromites shows that chromic sulphide,  $\text{Cr}_2\text{S}_3$ , reacts with the sulphides of many metals in the same manner as chromic oxide with the corresponding oxides. H. W.

**Tungstoborates.** By D. KLEIN (*Bull. Soc. Chim.* [2], **36**, 205—209).—When a solution of cadmium tungstoborate is evaporated in a vacuum, it yields large crystals, apparently rhombic, of the composition  $9\text{WO}_3 \cdot \text{B}_2\text{O}_3 \cdot 2\text{CdO} \cdot 2\text{H}_2\text{O} + 16\text{Aq}$ , which melt in their water of crystallisation at  $75^\circ$ , giving a somewhat mobile liquid of sp. gr. 3·6. Although the salt crystallises readily, it is extremely soluble in water, 100 parts of the salt dissolving in 8 parts of water at  $19^\circ$ . The solution has a sp. gr. 3·28. By means of this salt, solutions can be obtained of any sp. gr. between 1 and 3·6, by the use of which the majority of ordinary minerals may be mechanically separated. The author has obtained the following compounds:—

*Cobalt tungstoborate*,  $9\text{WO}_3 \cdot \text{B}_2\text{O}_3 \cdot 2\text{CoO} \cdot 2\text{H}_2\text{O} + 16\text{Aq}$ , a deep red, somewhat soluble salt, giving a solution of sp. gr. 3·32 at  $19^\circ$ .

*Nickel tungstoborate*,  $9\text{WO}_3 \cdot \text{B}_2\text{O}_3 \cdot 2\text{NiO} \cdot 2\text{H}_2\text{O} + 16\text{Aq}$ , a dark green salt, almost as soluble as the cadmium compound.

*Copper tungstoborate*,  $9\text{WO}_3 \cdot \text{B}_2\text{O}_3 \cdot \text{CuO} \cdot 2\text{H}_2\text{O} + 16\text{Aq}$ , forms clear blue crystals, which dissolve in one-fifth of their weight of water at  $10^\circ$ , lose their colour at  $165^\circ$ , and become yellow when ignited.

*Manganese tungstoborate*,  $9\text{WO}_3 \cdot \text{B}_2\text{O}_3 \cdot 2\text{MnO} \cdot 2\text{H}_2\text{O} + 15\text{Aq}$ , rose-coloured crystals, which alter rapidly when exposed to air. Sp. gr. of solution at  $19^\circ = 3\cdot15$ .

*Dichromic tungstoborate* ( $9\text{WO}_3 \cdot \text{B}_2\text{O}_3$ ) $_3 \cdot 2\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + 69\text{Aq}$ , obtained by the decomposition of dibarium tungstoborate with chromium sulphate, crystallises from a syrupy solution with some difficulty in small crystals.

*Lead tungstoborate*,  $9\text{WO}_3 \cdot \text{B}_2\text{O}_3 \cdot 2\text{PbO} \cdot 2\text{H}_2\text{O} + 9\text{Aq}$ , obtained by the action of a cold dilute solution of tungstoboric acid on lead carbonate, is somewhat less soluble than the preceding salts, and does not give a solution of very high sp. gr.

*Uranic tungstoborate* ( $9\text{WO}_3 \cdot \text{B}_2\text{O}_3$ ) $_2 + (\text{U}_2\text{O}_3)_3 + 31\text{Aq}$ , obtained by the decomposition of the dibarium salt by uranium sulphate in presence of hydrochloric acid, forms hard crusts adhering firmly to the sides of the dish. Its constitution has not yet been determined. Apparently the salt,  $9\text{WO}_3 \cdot \text{B}_2\text{O}_3 \cdot 2\text{U}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + n\text{Aq}$ , does not crystallise. The normal salt could not be obtained.

The thallium and silver salts form very slightly soluble crystalline powders, containing 3 and 12 mols.  $\text{H}_2\text{O}$  respectively.

*Cerium tungstoborate*,  $9\text{WO}_3 \cdot \text{B}_2\text{O}_3 \cdot 2\text{CeO} \cdot 2\text{H}_2\text{O} + 17\text{Aq}$ , which forms rose-coloured very soluble crystals, and the magnesium salt, containing 20 mols.  $\text{H}_2\text{O}$ , may also be obtained by double decomposition.

The ammonium salt forms small octahedrons, which very rapidly effloresce when exposed to the air. The potassium compound has already been described. The barium salt crystallises with 13 mols.  $\text{H}_2\text{O}$  in quadratic octahedrons, very soluble in warm, but less soluble in cold water. The disodium salt crystallises with 9 mols.  $\text{H}_2\text{O}$  in rhombic octahedrons, very soluble in water, giving a solution of sp. gr. 2.5. The monosodium compound,  $9\text{WO}_3 \cdot \text{B}_2\text{O}_3 \cdot \text{Na}_2\text{O} \cdot 3\text{H}_2\text{O} + 20\text{Aq}$ , forms crystalline masses with octahedral cleavage. Its solution has a high sp. gr. Attempts to obtain tetrabasic tungstoborates have not yet been successful.

Tungstoboric acid may be readily obtained in yellowish octahedrons by decomposing dibarium tungstoborate with exactly the required amount of sulphuric acid. It gives a solution of very high sp. gr., and probably has the composition,  $9\text{WO}_3 \cdot \text{B}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + 18\text{Aq}$ . With salts of quinine, cinchonine, strychnine, and morphine, it gives white or yellowish-white precipitates, insoluble in acids in the cold. With salts of codethylen it gives an abundant yellowish precipitate, soluble in boiling nitric acid, but with methocodeine and ethylenemorphine it gives no reaction. With peptones it forms a coagulum, soluble in excess of the acid.

In all cases the boric acid was estimated by difference. It should also be borne in mind that very different formulæ correspond with differences in analytical results not greater than unavoidable errors of experiment.

C. H. B.

**Temperatures of Formation and Decomposition of Mercuric Oxide.** By W. H. ECHOLS (*Chem. News*, **44**, 189).—By the use of Carnelley's method for the estimation of high temperatures, it was found that mercuric oxide is first formed by direct union of mercury and oxygen at about  $450^\circ$ , and that it begins to be decomposed at about  $630^\circ$  under the ordinary atmospheric pressure. J. K. C.

**Mercurous Chloride.** By E. DRECHSEL (*J. pr. Chem.*, **24**, 46).—This salt dissolves in a solution of mercuric nitrate when warmed, forming mercuric chloride and mercurous nitrate. Hence mercurous nitrate is not precipitated by mercuric chloride in the presence of mercuric nitrate.

D. A. L.

**Bismuth Subnitrate.** By C. SCHNEIDER (*Arch. Pharm.* [3], **18**, 350—356).—Keeping in view the principles laid down by R. Schneider (*J. pr. Chem.*, **20**, 418—434), the author has prepared large quantities of basic bismuth nitrate free from arsenic. The principles are: bismuth arsenate is practically insoluble in a concentrated and as far as possible neutral solution of bismuth nitrate. For the complete oxidation of arsenic, an equable temperature of at least  $75$ — $90^\circ$  is necessary, and the resulting solution of the metal, as concentrated as possible, should contain as little free nitric acid as possible.

By dissolving 1 kilo. of (so-called pure) bismuth in coarse powder in small portions at a time in 5 kilos. of the purest nitric acid free from chlorine (sp. gr. 1.2) at  $80^\circ$ , and cooling on completion of the

action, a slight residue of basic salt and traces of metal remained undissolved, which residue was found to be perfectly free from arsenic. On evaporating and decomposing the crystals of normal bismuth nitrate obtained, the basic nitrate was found to be free from arsenic, but the water used for precipitating and washing contained arsenic, showing that arsenic must have been in the solution of the metal, which contained large quantities of pure nitric acid, and must subsequently have been retained by the crystals of the normal salt. Other experiments of a similar nature were made with slight variations, and gave substantially the same results. By operating in a precisely similar manner on 1 kilo. of the same bismuth—after purification by fusion with soda and potassium nitrate—precisely the same results as to arsenic were obtained. 100 grams of an arsenical bismuth, in coarse powder, were mixed with 0.5 gram of metallic arsenic, and then added in very small successive portions to 500 grams of nitric acid (sp. gr. 1.2), heated to 80°. The liquid was at once rendered turbid by the separated bismuth arsenate. The insoluble residue was white, weighing 2.3 grams, and was highly arsenical. 125 grams of normal salt were obtained, yielding 59 grams of basic salt. The mother-liquor was free from arsenic, but the basic salt gave very perceptible arsenic mirrors in Marsh's apparatus. 120 grams of the same coarsely powdered metal, with 0.5 gram of metallic arsenic, were acted on exactly as in the previous case, except that the metal was added quickly in small portions; the highly arsenical insoluble residue weighed 6 grams. 175 grams of normal salt were obtained, yielding 75 grams of basic salt, which, as well as the mother-liquor, was completely free from arsenic.

F. L. T.

**Absorption of Chlorine by Arsenious Chloride, and the Amount retained at Various Temperatures.** By B. E. SLOAN (*Chem. News*, 44, 203).—All attempts to produce an arsenic pentachloride having failed, it nevertheless seemed worth while to examine the effect of exposing the trichloride to gaseous chlorine at low temperatures, observing to what extent the gas was absorbed, and whether any indications could be obtained of true chemical combination. Pure arsenic trichloride was prepared by the direct action of chlorine on the metal, and placed in a long-necked flask, immersed in a properly protected bath of crushed ice and hydrochloric acid and chlorine gas, well dried and previously cooled, was slowly bubbled through for eight hours, maintaining throughout a temperature of  $-23^{\circ}$  under ordinary pressure (about 745 mm.). At the end of this time, about 20 c.c. of the liquid was drawn off into another cooled flask, using a special arrangement of tubes to prevent any gaseous chlorine being brought with it, and to obviate any general contact with the atmosphere. This receiving flask with its appurtenances was then again weighed, so that the exact amount of the chloride introduced was known. This was mixed with a strong solution of soda, contained in one of the above-named tubes, the mixture diluted to a definite volume, and the chlorine and arsenic were determined in separate portions of this. The results showed 4.447 atoms chlorine for 1.0 arsenic. As a lower temperature could hardly have been used without

risk of liquefying the chlorine itself, and as experiments showed that the time employed was much more than sufficient to allow of all the gas being taken up that would dissolve, it was obvious that a pentachloride had not been formed.

D. B.

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## Mineralogical Chemistry.

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**Native Gold from Virginia.** By S. PORCHER (*Chem. News*, **44**, 189).—Externally the grains have the appearance of fine gold, but the interior is white. On analysis, the atomic proportion of gold to silver was found to be 100:94·9; and allowing for the partial removal of silver which the surface has experienced, the alloy seems in all probability to consist of single atoms of the two metals, and may be represented as AuAg. J. K. C.

**Analysis of Wulfenite from Ruby Hill, Eureka Co., Nevada.** By C. L. ALLEN (*Chem. News*, **44**, 203).—The material, formerly found in large quantity, is well crystallised, of a bright orange-yellow colour, and sp. gr. = 6·701. Analysis gave:—

MoO <sub>3</sub> .	PbO.	CuO.	Fe <sub>2</sub> O <sub>3</sub> .
39·33	61·11	1·04	0·38 = 101·86
D. B.			

**Sodium Alum of Japan.** By E. DIVERS (*Chem. News*, **44**, 218).—A natural sodium alum, occurring as an efflorescence on decomposing sodium felspar, with pyrites scattered through it, is found in the province of Idzumo, in the prefecture of Shimané, Japan. It is an alum of the normal type, crystallising with 24H<sub>2</sub>O, as is seen from the analysis:—

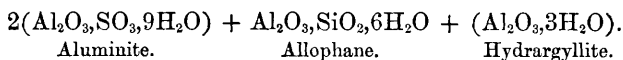
Al <sub>2</sub> O <sub>3</sub> .	Na <sub>2</sub> O.	SO <sub>3</sub> .	H <sub>2</sub> O (by diff.).
11·27	7·26	34·73	46·74 Found.
11·23	6·76	34·90	47·11 Calculated Al <sub>2</sub> Na <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·24H <sub>2</sub> O.

The large excess of sodium found is probably due to the presence of ammonium sulphate, owing to an imperfect ignition. Mendozite, from South America, is referred by Dana to a class of alums with 22 mols., and by Rammelsberg to alums with 20 mols. H<sub>2</sub>O.

L. T. O'S.

**Occurrence of a Mineral in the Courl Mine in Westphalia.** By F. MUCK (*Chem. Centr.*, 1881, 199).—A layer of a pure white slime was found on the bottom of a cross cut in the mine of Courl, which had been under water for one year, and then dried up. The mineral substance represented a homogeneous mass 0·5 m. in thickness, having a saline taste. Analysis of the substance dried over sulphuric acid gave numbers corresponding with the proportion of

$10\text{Al}_2\text{O}_3 : 2\text{SO}_3 : \text{SiO}_2 : 45\text{H}_2\text{O}$ , which gives the following rational formula:—



Aluminite.

Allophane.

Hydrargyllite.

D. B.

**Chrome Iron Ore of Japan.** By E. DIVERS (*Chem. News*, **44**, 217—218).—This ore, obtained from Oita Prefecture, Japan, is massive, of sp. gr. 4·5, hardness 5·5, and of a grey-black colour, being brown only where weathered. Its fracture is slaty, partly crystalline, and shows numerous large faces, inclined at all angles; lustre resinous to submetallic; powder brown. On the faces of natural fractures there are deposits of a greyish-pink, but nearly white, soft, and unctuous mineral. On heating, the ore gains in weight, and then contains only a trace of magnetic matter; 2·53—2·87 per cent. dissolves in acid. The following are the analyses:—

I. *Whole Ore, air-dried.*

		1.	2.	Mean.
Cr <sub>2</sub> O <sub>3</sub> .....		59·39	59·20	59·3
FeO.....		28·32	28·22	28·27
FeCr <sub>2</sub> O <sub>4</sub> .	Fe <sub>3</sub> O <sub>4</sub> .	MgO.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .
87·30	0·29	9·17	1·58	0·80 = 99·14

II. *Portion decomposed by Hydrochloric Acid.*

	$\text{Cr}_2\text{O}_3$ .	Fe as $\text{Fe}_2\text{O}_3$ .	$\text{MgO}$ .	$\text{Al}_2\text{O}_3$ .	$\text{SiO}_3$ .
1 .....	0·32	0·53	1·17	0·51	—
2 .....	0·38	0·55	1·44	0·50	—
Mean....	0·35	0·54	1·30	0·51	1·30

Part of the iron dissolved in the ferrous state.

III. *Pinkish-white Mineral (after allowing for 36·5 per cent. admixed Chrome Iron Ore).*

$\text{SiO}_2$ .	$\text{MgO}$ .	$\text{Al}_2\text{O}_3$ .	$\text{H}_2\text{O}$ (by ignition).
32·6	28·7	27·4	11·3

The ore appears to be nearly pure ferrous chromite, the insolubility of the iron in acid showing that it is united with the chromium oxide; and from the large proportion of magnesia present, the author considers it to have the formula  $\text{MgO} \cdot 2\text{FeO} \cdot 2\text{Cr}_2\text{O}_3$ , or to be  $3\text{FeO} \cdot 2\text{Cr}_2\text{O}_3$ , in which 1 mol.  $\text{FeO}$  is replaced by  $\text{MgO}$ . This is borne out by the author's results.

*Almost Insoluble.*

	Calculated for MgO.2FeO.2Cr <sub>2</sub> O <sub>3</sub> .	Found.
Cr <sub>2</sub> O <sub>3</sub> .....	59.3	59.30
FeO .....	28.0	27.90
MgO.....	7.78	7.93

*Soluble.*

MgO.2FeO.2Cr <sub>2</sub> O <sub>3</sub> .....	0.57
Hydrated magnesium aluminium silicate .....	3.62
Magnetite .....	0.29
	<hr/>
	99.04

L. T. O'S.

**Felspar from Rhombic Porphyry of Christiania.** By O. MÜGGE (*Jahrb. f. Min.*, 1881, 2, Mem., 107—120).—This rock is distinguished by large inclosed felspar crystals, which, splitting parallel to the two cleavage-faces, appear with an acute rhombic outline. The two cleavage-faces generally differ somewhat in lustre and hardness, but cannot always be thus distinguished. The crystals examined in section are found to be almost completely decomposed. These crystals occur also in other rocks in the neighbourhood. The rock has often been examined since L. v. Buch described it, but without a satisfactory result. The crystals from various localities used by the author showed the faces  $\infty P.2P\infty$ , and sometimes  $\infty R\infty$ , but  $0P$  as a natural face was entirely absent. The plane angle on the  $\infty R\infty$  cleavage-face (*i.e.*,  $\infty P\infty : 2P\infty$ ) is  $142^{\circ}$ — $144^{\circ}$ , and that of  $0P : 2P\infty$  is  $79^{\circ}$ — $86^{\circ}$ ; the corresponding angles on orthoclase are  $144^{\circ} 15'$  and  $80^{\circ} 8'$ ; the angle contained by the prismatic faces was, however, always greater than  $118^{\circ} 47'$ , *viz.*,  $127^{\circ}$ — $133^{\circ}$ ; but all the faces, it must be noted, are rounded at the edges. The crystals are twinned in such a manner that  $\infty P\infty$  is both twin- and contact-plane; the half angle enclosed by the two  $0P$  cleavage-faces varies from  $64^{\circ} 10'$  to  $63^{\circ} 16'$ , which agrees well with the angle  $\beta = 63^{\circ} 57'$  of orthoclase; the two adjacent  $\infty R\infty$  faces give a single though indistinct image, and certainly their inclination does not amount to  $7^{\circ}$ — $8^{\circ}$ , as in the albite-anorthite group of feldspars. The author has never observed the twin-plane  $\infty P$ , nor  $\infty R\infty$ . As regards the latter, a very fine striation was in one case observed on  $0P$ , but with difficulty, owing to the oscillatory cleavages parallel to  $0P$  and  $\infty R\infty$ , and moreover the twin laminae could not be optically detected. A further proof of the monosymmetrical character of the crystals is that the angle  $0P : \infty R\infty$  lies between  $88^{\circ} 50'$  and  $91^{\circ} 16'$ ; and although the reflections are not sharp, yet it is certain that angles of  $87^{\circ}$ — $86^{\circ}$  and of  $93^{\circ}$ — $94^{\circ}$  are quite excluded. So far these crystals have been considered as orthoclase, but that this is not so the author shows optically and chemically. From still fresh crystals, sections were cut parallel to  $0P$  and to  $\infty R\infty$ , and also perpendicular to both these planes (*i.e.*, parallel to a face  $mP\infty$ ). The depolarising direction in the sections parallel to  $0P$  is slightly inclined to the edge  $0P : \infty R\infty$ , *viz.*,  $1^{\circ}$ — $2^{\circ}$ , and in the sections



parallel to  $\infty P\infty$ , the similar angle is nearly  $0^\circ$ , and never exceeds  $3^\circ$ ; in neither case can twin lamellæ be detected. All sections parallel to  $mP\infty$  show twin lamellæ, whose depolarising directions are inclined about  $28-29^\circ$  to each other, but vary from  $10^\circ$  to even  $36^\circ$ ; and again, excessively fine lamellæ, perpendicular to the others. Sections lying between  $0P$  and  $mP\infty$  show depolarising directions inclined at intermediate angles. A section from a twin crystal parallel to  $\infty R\infty$  showed the depolarising directions to be almost parallel, and perpendicular to the cleavage lines parallel to  $0P$ , *i.e.*, they formed together an angle of  $47\frac{1}{2}^\circ$  (with orthoclase =  $52^\circ 6'$ ). The optical axial angle could not be measured, owing to the numerous enclosures. The author discusses previous analyses, which would show that the mineral is neither orthoclase, nor a normal mixture according to Tschermak's theory. In order to decide whether this body has an anomalous composition, or whether the observed variations are due to very impure material used, carefully selected pieces were taken for analysis. These were powdered and fractionated by Thoulet's solution, about 1 gram of light grey powder of sp. gr. 2.651 being obtained, which had practically the composition required by oligoclase; the heavier particles contained numerous enclosures of iron oxide, mica, and serpentine. Analyses on raw materials differ from the preceding, but approach nearer on partial purification. All these data point to the crystals being oligoclase, and the enclosing rock, instead of being a quartz-free porphyry or syenite, must be considered as a diabase, and more particularly an olivin-diabase. In conclusion, the author remarks that these oligoclase crystals occur in two species of rocks, one containing olivin and apatite crystals, and massive mica and augite; the other rock containing, however, no olivin, but little apatite, and the mica in crystals, so that up to this time, under the term "rhombic porphyry" different rocks have been included.

H. B.

**Analysis of Felspar accompanying Microlite in Amelia Co., Virginia.** By B. E. SLOAN (*Chem. News*, 44, 207).—In the vein of coarse granite, about a mile from Amelia Court-house, where large sheets of mica are obtained, and the rare mineral microlite is found along with brilliantly phosphorescent fluor spar, columbite and great crystals of beryl, there occur crystalline masses of a beautiful felspar, nearly white with faint bluish-green tinge, highly cleavable, with a brilliant vitreous, slightly pearly lustre on the principal cleavage-faces; sp. gr. = 2.501. The general appearance is that of oligoclase from some localities, but the author's analysis shows that the mineral is orthoclase. He found—

			Atomic ratios.
SiO <sub>2</sub> .....	65.37	—	1.0895—5.96
Al <sub>2</sub> O <sub>3</sub> .....	18.74	0.1837	} 0.1845—1.01
Fe <sub>2</sub> O <sub>3</sub> .....	0.13	0.0008	
CaO .....	0.27	0.0048	} 0.1828—1.00
K <sub>2</sub> O .....	12.98	0.1378	
Na <sub>2</sub> O .....	2.49	0.0402	
<hr/>			
99.98			

agreeing closely with the normal tri-silicate formula.

D. B.

**Analysis of Epidote from near Greenwood, Albemarle Co., Virginia.** By T. P. LIPPIT (*Chem. News*, **44**, 208).—This mineral is of clear, characteristic pistachio-green colour; sp. gr. = 3.39. Analysis of the mineral dried at 100° gave—

SiO <sub>2</sub> .....	39.74	—	0.6623 = 9
Al <sub>2</sub> O <sub>3</sub> .....	21.55	0.2113 }	0.3069 = 4.17
Fe <sub>2</sub> O <sub>3</sub> .....	15.29	0.0956 }	
CaO.....	22.75	0.4062 }	0.4214 = 5.73
MgO.....	0.61	0.0152 }	
<hr/>			
99.94			

agreeing with the normal ortho-silicate formula  $M''_6R'''_3Si_3O_{36}$ —about two-thirds aluminium epidote, and one-third iron epidote. The whole of the iron is present in the ferric state. D. B.

**A Zinc-bearing Clay from the Neighbourhood of the Bertha Zinc Mine, Pulaski Co., Virginia.** By B. H. HEYWARD (*Chem. News*, **44**, 207).—It occurs at the above locality in a seam several inches thick, overlying the deposit of calamine. It is light reddish-yellow in colour, cuts under the knife like meerschaum, and on a cut surface exhibits a grained texture, like that of wood. With water it forms a plastic mass, which is tenacious, becomes rigid on drying, and hard in the fire. Analysis gave—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	ZnO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.
37.38	24.67	6.34	12.10	0.27	0.47	0.27	17.04

The zinc probably exists in the form of silicate in fine subdivision, and uniformly mixed with the aluminous silicate of the clay. D. B.

**Constitution of the Water of the Dead Sea.** By H. FLECK (*Chem. Centr.*, 1881, 427).—The water has a sp. gr. of 1.1861; neutral reaction; contains neither free nor combined carbonic acid; was slightly turbid, and gave on analysis—

	KCl.	NaCl.	NaBr.	MgCl <sub>2</sub> .	CaCl <sub>2</sub> .	CaSO <sub>4</sub> .
Grams in 1 kilo...	14.250	62.438	4.236	108.015	29.811	1.021
Grams in 1 litre ..	16.900	74.051	5.024	128.105	35.355	1.211

Ammonia, silicic acid, and ferric oxide were also found qualitatively. D. B.

**Mother-liquor of the Allendorf-on-Worra Salt Works.** By E. REICHARDT (*Arch. Pharm.* [3], **18**, 187—189).—The analysis of this liquor, which was yellow, perfectly clear, of slightly alkaline odour, sp. gr. 1.285, and neutral reaction, gave in 100 grams of the liquor—

	Grams.
SiO <sub>2</sub> .....	0·0039
Cl .....	15·6672
Br .....	0·0603
SO <sub>3</sub> .....	3·5440
CaO .....	0·0280
MgO .....	4·1420
K .....	1·8046
Na .....	2·9933
Li .....	0·0022
Organic matter .....	0·9040

29·1495

F. L. T.

**Examination of the Mother-liquors from Salt Brines of West Virginia for Iodine.** By A. L. BAKER (*Chem. News*, **44**, 207).—With a view of testing the accuracy of a statement made some time ago that the “bitterns” left from the manufacture of salt by boiling the natural brines of West Virginia and Eastern Ohio, which have furnished very large quantities of bromine, contain, in addition to this element, about one-third its weight of iodine, the author analysed the following samples of bittern:—

No. 1. Snow Hill Furnace, Kanawha Co., W. Va., sp. gr. = 1·305.

No. 2. Daniel Boom Furnace, Kanawha Co., W. Va., sp. gr. = 1·270.

No. 3. Newcastle Furnace, Mason Co., W. Va., sp. gr. = 1·300.

No. 4. Hartford City Furnace, Mason Co., W. Va., sp. gr. = 1·285.

	Free acid counted as HCl, mgrms. per litre.	Free iodine, mgrms. per litre.	Iodine in iodides, mgrms. per litre.	Total iodine, mgrms. per litre.
No. 1 .....	2400	59·2	—	59·2
No. 2 .....	200	1·8	38·2	40·0
No. 3 .....	100	12·2	40·0	52·2
No. 4 .....	400	12·4	26·0	38·4

D. B.

**Examination of the Ambrosiusbrunn-Quelle, Marienbad, Bohemia.** By W. F. GINTL (*J. pr. Chem.*, **24**, 25—38).—The discharge from the outlet on the west side of the spring is 439·2 litres an hour (bar. 747 mm.). The temperature of the spring is 9·6° taken at a depth of 0·5 meter and when temperature of air = 19·8°. The water is colourless (when seen in great thickness very slightly yellowish) and odourless. Its taste is at first pleasant, sharp, and saline, but afterwards strongly inky. The fresh water reacts slightly acid; after boiling it turns milky and alkaline, whilst a red-brown precipitate separates out, and carbonic anhydride is given off. It sp. gr. is 1·0013 at 14·2°. The analysis compared with that made by Raysky in 1860 is as under:

	In 10,000 parts of water.	
	Raysky.	Gintl.
Potassium sulphate . . . .	traces	0·34588
Sodium sulphate . . . . .	1·889	3·11345
Sodium chloride . . . . .	0·499	0·13782
Sodium carbonate . . . . .	0·958	0·58400
Lithium carbonate . . . . .	traces	0·00424
Calcium carbonate . . . . .	2·424	2·08500
Magnesium carbonate ..	1·104	1·89464
Ferrous carbonate . . . . .	0·439	1·20849
Manganous carbonate ..	0·029	0·01830
Silica . . . . .	0·470	0·49860
Free and half-combined carbonic acid . . . . .	20·633	25·56321
Extracted matter . . . . .	0·023	—

The gas from the spring contains in 1000 c.c. at 0° and 760 mm.—  
 carbonic anhydride 954·8 c.c., oxygen 16·2 c.c., nitrogen (and a trace  
 of hydrocarbon) 29·0 c.c.

D. A. L.

## Organic Chemistry.

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**Possibility of Artificially Preparing Amorphous Elementary Carbon Free from Hydrogen, Oxygen, and Nitrogen.** By S. PORCHER (*Chem. News*, **44**, 203).—It is an interesting question, whether hydrogen, oxygen, and nitrogen exist in chemical union with black amorphous carbon—prepared from any form of organic matter as a residue from destructive distillation or imperfect combustion—or are retained by surface attraction only; such surface condensation undoubtedly occurs to a large extent on exposure to the atmosphere, but much, if not all, of the gases so condensed may be driven off again by heat. With a view of obtaining some light on this question, it was proposed that carbon should be prepared from materials altogether free from the elements in question; that its weight should be determined; and that it should then be exposed to the atmosphere, heated again, and the product, after cooling, examined as to the presence of any of the three other elements named, hydrogen, if found, being of course attributable to vapour of water.

The carbon was prepared by passing the vapour of carbon tetrachloride through a hard glass tube containing metallic sodium very carefully freed from any traces of naphtha, taking care to expel all air before heating the metal. After much trouble, the author succeeded in obtaining a product which was almost perfectly free from impurities. It was then heated to a temperature not much below that at which it would have begun to burn, and afterwards burned in a platinum boat in a stream of very carefully purified and well dried oxygen, the products of combustion being collected as in ordinary organic analysis; one

specimen gave absolutely no water, thus indicating the absence both of condensed aqueous vapour and of combined hydrogen, whilst a minute loss on the weight of the original material was probably attributable to the carbon not being completely burned, traces being retained in the ash, which was in this case present in considerable amount. D. B.

**Decomposition of the Hydrocarbons from American and Caucasian Petroleum at Low Temperatures.** By G. GUSTAVSON (*Chem. Centr.*, 1881, 1353).—When a current of hydrobromic acid gas is passed through a solution of aluminium bromide in the above hydrocarbons, the liquid separates into two layers, of which the lower **always** consists of the compound  $\text{AlBr}_3\cdot\text{C}_4\text{H}_8$ , identical with that obtained by the action of ethyl bromide on aluminium bromide. It is a viscid orange-yellow liquid, which does not solidify at  $-15^\circ$ , and undergoes no change at  $100$ – $120^\circ$ , but is decomposed at a higher temperature with evolution of gaseous hydrocarbons. It is insoluble in the hydrocarbons and carbon bisulphide, but is miscible in all proportions with ethyl bromide. It is decomposed by the action of water, whereby not only the aluminium bromide, but also the organic substance, undergoes chemical change. The more complicated the hydrocarbon the more easily does the reaction occur.

In this reaction a number of gaseous hydrocarbons are formed in addition to the  $\text{AlBr}_3\cdot\text{C}_4\text{H}_8$ , especially if the aluminium bromide is present in excess. They cannot be condensed in a freezing mixture, and consist of lower saturated hydrocarbons, together with some which are unsaturated, the proportion of the latter varying with the conditions of the reaction. The hydrobromic acid appears to play an important part in the reaction; *e.g.*, hexane is decomposed thereby into ethyl bromide and butane, hydrobromic acid being reproduced as soon as the former enters into reaction with the aluminium bromide, so that the action of the hydrobromic acid begins afresh.

Mendelejeff has already (*Chem. Centr.*, 77, 243) endeavoured to explain the existence of methane in petroleum by the decomposition of the liquid hydrocarbons into methane and unsaturated hydrocarbons, and this is probably accelerated by the presence of hydrogen chloride or bromide, since metallic chlorides, and probably bromides, always occur in nature with petroleum. T. C.

**Crystalline Guanine.** By E. DRECHSEL (*J. pr. Chem.*, 24, 44–45).—Guanine freshly precipitated by ammonia from its solution in hydrochloric acid, is added in small portions at a time, to a large quantity of ammonia heated to about  $30$ – $35^\circ$ : the solution is filtered and the ammonia allowed to evaporate gradually in the air, when small crystals, apparently rhombic needles or plates, separate out. These crystals show all Capranica's reactions for guanine. D. A. L.

**Crystalline Compounds of Calcium Chloride with Alcohols.** By J. B. HEINDL (*Monatsh. Chem.*, 1881, 200–211).—The author has reinvestigated the compounds of calcium chloride with ethyl alcohol, isobutyl alcohol, and fermentation amyl alcohol, and assigns to them

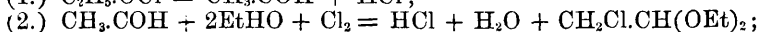
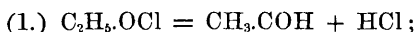
the formulæ  $\text{CaCl}_2, 3\text{C}_2\text{H}_5\text{O}$ ;  $\text{CaCl}_2, 3\text{C}_4\text{H}_{10}\text{O}$ ; and  $\text{CaCl}_2, 3\text{C}_5\text{H}_{12}\text{O}$ . He failed to confirm the existence of compounds containing both alcohol and water, and attributes the discrepancies of the former analyses to the methods employed in drying the crystals, it being necessary in this to attend to the precautions already detailed in Lieben's paper on compounds of calcium chloride with the fatty acids (Abstr., 1881, 712).

A. J. G.

**Action of Chloride of Lime on the Alcohols.** By Dr. A. GOLDBERG (*J. pr. Chem.* [2], **24**, 97—119).—I. *Action on Ethyl Alcohol*.—Schmitt and the author have previously shown that equivalent quantities of chloride of lime and alcohol, when mixed, become heated, and there distils over much unaltered alcohol and a greenish-yellow oil, which by the action of light or heat decomposes almost explosively, with evolution of chlorine, hydrochloric and hypochlorous acids. The products of the decomposition, treated with water, gave an aqueous solution of aldehyde, and an insoluble oil containing much monochloroacetal and a little chloroform and dichloroacetal; further, the oil seemed to contain a definite body boiling at  $77-78^\circ$ . The author has confirmed all these statements except the last, the liquid of constant composition and boiling point really consisting of several compounds.

A large quantity of the above oil, insoluble in water, was fractionally distilled, when monochloroacetal, passing over between  $150$  and  $160^\circ$ , and dichloroacetal at  $185-190^\circ$ , were obtained; crotonchloral (b. p.  $163-165^\circ$ ), and acetal (b. p.  $90-120^\circ$ ), could not be detected. The portions boiling between  $70^\circ$  and  $150^\circ$  were separated into two portions, one boiling at  $70-80^\circ$ , and the other above  $150^\circ$ , without any intermediate portion. Of the portion boiling  $70-80^\circ$ ,  $\frac{3}{4}$  litre was used for further fractionations; a small portion distilled below  $70^\circ$ , but the principal portions between  $72-73^\circ$ , and between  $77-78^\circ$ , the percentages of chlorine in these fractions being  $70.5$  and  $34.0$ . Sodium acted energetically on the latter, but scarcely at all on the former, which was found to be scarcely altered in composition by distillation over sodium. The distillate heated under pressure with hydrochloric acid, yielded a black resinous body and an oily liquid, boiling entirely between  $60-65^\circ$ , containing  $87.5$  per cent. chlorine, and having a vapour-density of  $4.24$ ; it is chloroform. The author is not able to determine whether this chloroform exists ready formed in the oil, or whether it is formed during the heating with hydrochloric acid, since all fractions of the oil give the phenylcarbamine reaction; they moreover all give a mirror with silver solutions, and when shaken with water impart to it an aldehyde-like smell, so that the oil also contains some higher aldehyde.

Considering the small quantity of oil insoluble in water formed, in some cases absolutely none, it is evident that the formation of the monochloroacetal is secondary to that of the aldehyde. The author, supposing the original oil before explosion to be ethyl hypochlorite, explains the reaction thus:—



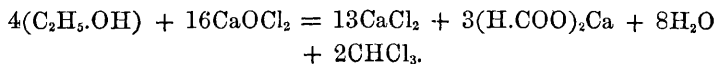
the unaltered alcohol in the second equation being that driven over by the energy of the reaction.

The action of *chloride of lime* on monochloroacetal was studied in order to get a clue to the formation of chloroform as above mentioned. With pure monochloroacetal, a reaction first took place on the water-bath, a greenish-yellow distillate passing over. This soon decomposed, no longer however violently, with evolution of chlorine and hydrochloric acid gas, and separated into two layers, an aqueous hydrochloric acid and an oily chlorinated body. This latter contained much unaltered monochloroacetal, but also di- and trichloroacetal, which were isolated and identified by their composition, and the latter by its yielding chloroform on distillation with potassium hydroxide.

After the action of equivalent quantities of alcohol and chloride of lime, the whole of the available chlorine is generally found to be exhausted; when twice the above quantity of alcohol was used with the same quantity of chloride of lime, but very little more product was obtained, but it contained much more of the low boiling bodies (*i.e.*, 70—80°).

*Action of chloride of lime on dilute alcohol.* Equivalent quantities of chloride of lime and alcohol, the latter diluted with its own volume of water, when mixed, reacted on each other in about 7 minutes, and the oily distillate decomposed violently; the oily products of the decomposition contained 3·4 per cent. crude chloroform, boiling 60—70°. With twice the above quantity of water the reaction commenced after 12—15 minutes, and the product contained 56·5 per cent. liquid, boiling 60—70°, and above 100° only a few drops of a liquid smelling strongly of monochloroacetal passed over. With three times the quantity of water, the distillation did not commence until after three-quarters of an hour, and was then imperfect; the product all distilled between 60 and 65°. With eight times the quantity of water the reaction commenced in three-quarters of an hour, and had to be finally assisted by gentle heating, the product distilling over below 70°; and, lastly, with a very large quantity of water, as in the manufacture of chloroform, the product distilled entirely between 60 and 63°. In 2 litres of chloroform residues of high boiling point obtained from the manufacturer, no trace of monochloroacetal could be detected.

These experiments show that on addition of water the quantity of monochloroacetal—the lowest chlorinated product—decreases rapidly, whilst that of the lower-boiling, but more highly chlorinated chloroform, increases as rapidly. The formation of traces of chloroform when absolute alcohol is used, the author considers to be due to the moisture in the chloride of lime, and that the addition of water, by diminishing the energy of the action, allows the chloride of lime to act further on the chlorinated acetal or chlorinated aldehyde, resolving it into chloroform and formic acid. But judging from the fact that from 1 kilo. alcohol only 1 kilo. chloroform can be obtained, it is probable that but one quarter of the total carbon goes to the formation of the chloroform, thus:—





II. *Action of Chloride of Lime on Chemically Pure Methyl Alcohol.*—Equivalent quantities were used, but no reaction took place spontaneously. When the mixture was heated on a water-bath, a distillate was obtained smelling of hydrochloric and hypochlorous acids and chlorine; it did not decompose violently, and dissolved completely in water, with evolution of a gas which exploded on applying a light. The aqueous solution contained neither chloroform nor aldehyde. This, which is in accordance with the observations of others, bears out the opinion that the chlorine never enters the carbinol residue, which is oxidised to formic or carbonic acid.

III. *Action of Chloride of Lime on Isopentyl Alcohol.*—On mixing equivalent quantities, the distillation commenced in about three-quarters of an hour, and considerable evolution of chlorine and hydrochloric acid gases took place. The receiver contained a light oil, floating on the aqueous hydrochloric acid. This oil on fractionation yielded (1) a portion boiling up to 100°, (2) a portion consisting mainly of isopentyl alcohol, and (3) a portion boiling, with decomposition, above 170°. Fraction (1) treated with acid sodium sulphite was found to contain valeral and an oil, probably butyl chloride, as its composition nearly approaches that of the latter; it is formed, together with formic acid, by the combined oxidation and chlorination of the alcohol. Fraction 3, by distillation under reduced pressure, yielded impure isopentyl isovalerate, boiling at 180–190°. The author has not been able to isolate the higher-boiling and chlorinated products.

H. B.

**Inversion of Sugar at the Ordinary Temperature.** By F. URECH (*Bied. Centr.*, 1881, 570).—A solution of cane-sugar is gradually inverted at the ordinary temperature, by the addition of 10 per cent. of hydrochloric acid. The inversion requires seven hours for completion, whereas at 70° a quarter of an hour suffices.

E. W. P.

**Specific Rotation of Cane-sugar Dissolved in Methyl Alcohol and in Acetone.** By B. TOLLENS (*Bied. Centr.*, 1881, 570).

	Specific rotation [ $\alpha$ ] <sub>D</sub> .
Solution of sugar in water .....	66·667°
Ethyl alcohol and water .....	66·827
Methyl alcohol „ .....	68·628
Acetone „ .....	67·396

E. W. P.

**Supposed Conversion of Starch into Sugar by Water at a High Temperature.** By F. SÖXHLET (*Bied. Centr.*, 1881, 554—557).—Starch subjected to the action of water under high pressure at 149° is to a certain extent converted into sugar, but as the proportion of water increases, the amount of sugar formed decreases; this is not the case if an acid (lactic acid) is present. The reason is to be found in the fact that there is present in potato and wheat starch, a free acid (due to the process of manufacture), which when diluted

with water is less energetic in its converting power: the amount of this acid in various samples has been determined. Rice and maize starch are, however, alkaline. Neutral starch is not converted into sugar by water under high pressures and temperatures.

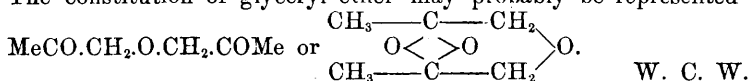
E. W. P.

**Cellulose and Coal.** By E. J. BEVAN and C. F. CROSS (*Chem. News*, **44**, 185—186).—By the action of sulphuric acid on the cellulose of jute fibre, a black substance resembling ordinary coal both in appearance and composition was obtained. It contained about 64 per cent. C, 4.2 per cent. H, and the remainder oxygen. By the action of chlorine on this body suspended in water, a yellow substitution-product was obtained smelling strongly of tetrachloroquinone, and similar in composition to the chlorinated bodies obtained from jute and esparto (*Jour. Chem. Soc.*, **38**, 666). From the fact that similar bodies are obtained from ordinary cannel coal, the authors think it probable that cellulose, peat, and the various kinds of coal are all members of the same series of compounds.

J. K. C.

**Glyceryl Ether.** By B. TOLLENS and A. LOE (*Ber.*, **14**, 1946—1950).—Glyceryl ether,  $C_6H_{10}O_3$ , has been prepared by Gegerfeld (*Ber.*, **4**, 919), Linnemann, and von Zotta (*Annalen*, Suppl., **8**, 257), and by Tollens (*Ber.*, **5**, 68). It is most readily obtained by distilling glycerol with 2 per cent. of ammonium chloride. That portion of the distillate which boils between  $220^\circ$  and  $270^\circ$ , is neutralised with potassium carbonate, and distilled in a current of steam. On the addition of potassium carbonate to the distillate, glyceryl ether rises to the surface as an oily liquid. When dried, it boils at  $170$ — $173^\circ$ .

The pure ether feebly reduces Fehling's solution, but after it has been treated with warm dilute hydrochloric acid, it acquires powerful reducing properties. After treatment with a warm acid, it yields iodoform when acted on by soda and iodine solution. The constitution of glyceryl ether may probably be represented as



W. C. W.

**Metaldehyde.** By HANRIOT and CECONOMIDES (*Compt. rend.*, **93**, 463—465).—Metaldehyde is insoluble in water, almost insoluble in alcohol, but somewhat soluble in aldehyde. The best solvents are chloroform and benzene, especially if heated. At ordinary temperatures the crystals undergo no alteration when exposed to the air. According to Kekulé and Zincke, when metaldehyde is heated in sealed tubes at  $112$ — $115^\circ$ , it is completely converted into aldehyde in a few hours, but the authors found that, even after heating for 40 hours at  $200^\circ$ , only half the metaldehyde was converted into aldehyde. When it is heated in a Toricellian vacuum, complete dissociation takes place after some time at  $180^\circ$ . By repeated distillations under atmospheric pressure, the metaldehyde can be entirely converted into aldehyde. This change takes place much more readily when the metaldehyde is dissolved in chloroform, especially if the latter is heated. The authors attempted to determine the vapour-density of metaldehyde by deter-

mining the vapour-density of the mixture of metaldehyde and aldehyde into which the former splits up when volatilised, and estimating the metaldehyde remaining unchanged on cooling. In this way they obtained numbers between 72.2 and 59.10, which point to the formula  $3C_2H_4O$ . Potassium hydrate and permanganate, chromic mixture, and ammonia are without action on metaldehyde. Chlorine at once converts it into ordinary chloral. C. H. B.

**Action of Hydrochloric Acid Gas on Isobutaldehyde.** By S. ŒCONOMIDES (*Bull. Soc. Chim.* [2], 36, 209—210).—When a current of dry hydrochloric acid gas is passed into well cooled isobutaldehyde, the latter is at once converted into a crystalline mass of para-isobutaldehyde, but after a time the crystals dissolve and the liquid separates into two layers. The passage of the gas is continued until the upper layer no longer increases. The lower layer consists of a saturated solution of hydrochloric acid, which when exposed to the air turns brown and deposits a thick black mass similar to that formed by the action of hydrochloric acid gas on aldehyde. The upper layer consists of a colourless, very thick oil, with a peculiar agreeable odour; b. p. 230—231° at 771.6 mm.; sp. gr. at 0° = 0.9575. It has the composition  $C_8H_{14}O$ , is converted into a resinous mass by the action of warm alkaline hydroxides, and reduces freshly precipitated moist silver oxide, giving the mirror characteristic of aldehydes. In ethereal solution, it instantly decolorises bromine, without evolution of hydrobromic acid. C. H. B.

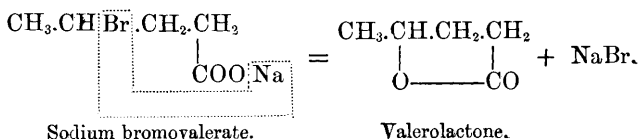
**Compound obtained in the Preparation of Isobutylal.** By S. ŒCONOMIDES (*Bull. Soc. Chim.* [2], 36, 210—211).—If in the preparation of isobutylal (Abstr., 1881, 711) the materials are not free from moisture, the addition of water to the product after it has been heated for some time on the water-bath, causes the separation of an oily layer, which, when dried and distilled, yields a colourless slightly viscid liquid (b. p. 223° at 756.8 mm.), with an agreeable ethereal odour different from that of acetal: sp. gr. at 0° = 0.9415. It has the formula,  $C_{10}H_{20}O_2 = CMe_2 : CH.O.CH(EtO).CHMe_2$ , and has probably been formed by the removal of hydrochloric acid from an intermediate product,  $CHMe_2.CHCl.O.CH(OEt).CHMe_2$ , by the free soda formed by the action of the water present on the sodium ethylate. When heated at 100° with twice its volume of hydrochloric acid, it yields monochlorethane and a resinous product. Its ethereal solution instantly decolorises bromine, but the product formed is apparently somewhat unstable, and has not yet been isolated. C. H. B.

**Constitution of Lactones.** By R. FITTIG (*Annalen*, 208, 111—121).—There are at present five simple lactones of the lactic acid series well known, viz.:—

	B. p.	M. p
Butyrolactone, $C_4H_6O_2$ . . . . .	201—203°	—18°
Valerolactone, $C_5H_8O_2$ . . . . .	206—207†	—
Caprolactone, $C_6H_{10}O_2$ . . . . .	220	—
Isocaprolactone, $C_6H_{10}O_2$ ..	207†	+7—8
Heptolactone, $C_7H_{12}O_2$ . . . . .	220†	+11

Their general properties are described in this Journal (38, 799); to these are now added the following:—The first two are soluble in all proportions in water, the last three are not so very soluble, and it is their solutions which are so sensitive to the changes of temperature between 0—80°. Alkaline carbonates as well as the hydroxides convert them into the corresponding hydroxy-acids, but not so quickly. These hydroxy-acids are all very unstable, and easily break up into water and the lactones. The barium and calcium salts are left as varnishes on evaporating their solutions, and are much less stable than the silver salts, which can easily be crystallised.

The author is of opinion that the researches on the lactones render the chemical process of their formation from the brominated acids quite clear, and he thus explains it. The bromine combines with the hydrogen or metallic atom in the carboxyl-group, and the liberated carbon and oxygen affinities satisfy one another, and restore the molecular equilibrium. The equation—



represents this change graphically.

Moreover, it is highly probable that those brominated acids in which the bromine-atom is combined with the third carbon-atom from the carboxyl-group (in the so-called  $\gamma$ -position) are easily broken up into lactones and metallic bromides (or hydrobromic acid) on neutralising with alkaline carbonates and boiling with water. In all lactones

the group  $\begin{array}{c} \text{C—C—C} \\ | \quad | \\ \text{O} \text{ — } \text{CO} \end{array}$  is present, and in the case of aromatic bodies,

the ortho-position is only of secondary importance. Coumarin is an exception. The paper concludes with some remarks on the constitution of pyroterebic, terebic, and terpenylic acids. D. A. L.

**Lactone of Normal Caproic Acid.** By R. FITTIG and E. HJELT (*Annalen*, 208, 67—71).—The lactone of normal caproic acid,  $C_6H_{10}O_2$  (this Journal, 38, 799), can be easily prepared at ordinary temperatures by mixing bromocaproic acid with water and adding a slight excess of an alkaline carbonate. On leaving the solution at rest for a few hours and saturating with potassium carbonate, the lactone separates as an oily layer.

When warmed or cooled its aqueous solution behaves similarly to that of the isocaproic derivative.

When boiled with baryta-water, it yields the hydroxycaproate  $(C_6H_{11}O_3)_2Ba$ , which is left as a colourless gum on evaporating the solution, and solidifies to an amorphous mass in the desiccator. It is deliquescent in the air, and is soluble in alcohol, but does not crystallise from the solution. On oxidation, this lactone yields succinic acid and traces of oxalic acid. By the action of ammonia on bromocaproic acid, even when heated with alcoholic ammonia in tubes at  $150^\circ$ , the lactone and not an amido-acid is formed. Isodibromocaproic acid from hydrosorbic acid also yields lactones when decomposed with water or an alkaline carbonate.

D. A. L.

**Lactone of Isocaproic Acid.** By J. BRET (*Annalen*, 208, 55—66).—The lactone of isocaproic acid (this Journal, 38, 315),  $C_6H_{10}O_2$ , is best obtained by the slow distillation of terebic acid, or by the oxidation of isocaproic acid with potassium permanganate. In addition to properties already described, the following may be added. It dissolves in two vols. of water at  $0^\circ$ , forming a clear solution, which becomes cloudy on warming; at  $30$ – $40^\circ$  it is white and opaque like milk, and deposits oily drops of the lactone. On further heating the turbidity clears off, and at  $80^\circ$  the solution is again clear and homogeneous; the same peculiarities are observed as the solution cools. Alkaline carbonates as well as the hydroxides convert it into hydroxyisocaproic acid; this acid can be isolated by decomposing its barium salt with hydrochloric acid in a freezing mixture; it is, however, very unstable, and readily breaks up into water and the lactone. Its *silver salt*,  $C_6H_{11}O_3Ag$ , crystallises from water in broad needles; it is easily soluble. By the action of sodium on the lactone in ethereal solution, a compound,  $C_6H_9NaO_2$ , is formed, from which the lactone is reprecipitated by acids.

On oxidising with dilute nitric acid, the lactone yields acetic acid and the monobasic acid,  $C_6H_8O_4$ , which forms colourless deliquescent crystals (m. p.  $68$ – $70^\circ$ ). It does not decompose at  $100^\circ$ . When warmed with carbonates, this acid yields salts of the dibasic *methyl-hydroxyglutaric acid*,  $C_6H_{10}O_5$ , of which it is the lactone.

The *calcium salt*,  $C_6H_9O_5Ca + 7H_2O$ , crystallises from boiling water on cooling in tufts of well-formed needles, which are not very soluble in cold water. It is precipitated from its aqueous solution by alcohol as a pure white precipitate. The *silver salt*,  $C_6H_9O_5Ag_2$ , forms a bulky slimy precipitate, which is scarcely soluble in hot water. This acid cannot exist in a free state, for as soon as it is separated from the salts it breaks up into water and its lactone.

The salts of the monobasic lactonic acid can be obtained by neutralising with carbonates in the cold; the *silver salt* is easily soluble in water, the *calcium salt* is not precipitated from its aqueous solution by alcohol.

It is possible that the crystals obtained by Markownikoff (*Annalen*, 182, 352) were not hydroxyglutaric acid, which, being the next lower homologue of the above acid, could not exist, but the lactonic acid,  $C_5H_6O_4$ .

D. A. L.

**Allylacetic Acid and Valerolactone.** By A. MESSERSCHMIDT (*Annalen*, **208**, 92—104).—Allylacetic acid prepared by the saponification of ethylic allylacetoacetate was found to agree in properties with that made by Zeidler (*ibid.*, **187**, 34), with the exception that it boiled at 187—189°, did not solidify at  $-18^{\circ}$ , and was not quite insoluble in water. Nascent hydrogen is without action on this acid. The *silver salt*,  $C_5H_7AgO_2$ , crystallises from its aqueous solution in colourless needles, which only discolour slowly in light. Hydrobromic acid converts allylacetic acid into *bromovaleric acid*,  $C_5H_9BrO_2$ , and the latter, when digested with boiling water until it is completely dissolved, decomposes and forms *valerolactone*,  $C_5H_{10}O_2$ , which is a colourless clear liquid, with a feeble but not unpleasant odour. It boils constantly at 206—207°†, does not solidify at  $-18^{\circ}$ , and is miscible with water in all proportions. The solution reacts neutral. By boiling it with baryta or lime-water, salts of *hydroxyvaleric acid* are produced. The lactone is reproduced when these salts are acidified.

The *barium salt*,  $(C_5H_9O_3)_2Ba$ , is a yellowish amorphous mass, soluble in water and absolute alcohol, and deliquescent in the air. The *calcium salt*,  $(C_5H_9O_3)_2Ca$ , is a white porcelain-like body, soluble in water and alcohol, and decomposes when heated at 100° with increasing loss of weight. Valerolactone yields succinic acid when oxidised with dilute nitric acid. 1 gram of lactone gives 0.268 gram succinic acid.

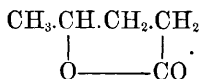
*Dibromovaleric acid*,  $C_5H_8Br_2O_2$ , may be made from allylacetic acid by mixing the latter very gradually with the theoretical quantity of bromine, both reagents being dissolved in dry carbon bisulphide. The new acid crystallises in colourless leaflets (m. p. 57—58°), very soluble in chloroform, benzene, and carbon bisulphide, sparingly soluble in light petroleum. Nascent hydrogen reconverts it into allylacetic acid, whilst the monobromovaleric acid under similar circumstances is converted into normal valeric acid.

*Bromovalerolactone*,  $C_5H_7BrO_2$ , is produced when dibromovaleric acid is decomposed by boiling with water for about two hours. It is a yellowish oily liquid, which cannot be distilled without decomposing, and does not solidify at  $-15^{\circ}$ . It dissolves slowly but completely in water, the solution has a neutral reaction, and the brominated lactone separates out on adding potassium carbonate.

By boiling with baryta, the brominated lactone decomposes, and *barium dihydroxyvalerate*,  $(C_5H_9O_4)_2Ba$ , is formed. It is precipitated from its aqueous solution by absolute alcohol as a thick white precipitate, which after a short time sets to a hard porcelain-like mass on the bottom of the vessel. There was not sufficient substance to prepare either the free acid or the oxylactone. D. A. L.

**Method of Preparation and Constitution of Valerolactone.** By L. WOLFF (*Annalen*, **208**, 104—110).—Valerolactone can also be prepared from levulic acid in the following way:—5 grams pure levulic acid are dissolved in 250 c.c. water, and a large excess of sodium amalgam (for each gram of acid used, 60 grams of 4 per cent. amalgam) added in the course of many days. When the evolution of hydrogen has ceased, the mercury is removed, the solution acidified with sulphuric acid, boiled, cooled, made alkaline with potassium car-

bonate, and then repeatedly shaken with ether. The residue left on distilling off the ether is dried with potassium carbonate, and then boils constantly at 206°. Its properties are the same as the above-described valerolactone; its sp. gr. at 0° was found to be 1.072. Besides the salts described above, *silver hydroxyvalerate*,  $C_5H_9O_3Ag$ , is here added. It crystallises from warm water in white, glistening, asymmetric needles, easily soluble in hot, but not very in cold water. This method of preparation shows that valerolactone has the constitution expressed by the formula—



Either Tollens' levulic acid from sugar candy, or Conrad's synthetical acetopropionic acid may be used, as both yield the same body on reduction. When the reduction of the levulic acid is conducted in acid solutions, the product is normal valeric acid. The yield is very good; this is the most economical and simple method yet known for the preparation of this acid.

D. A. L.

**Action of Nitric Acid on Brominated Fatty Bodies.** By J. KACHLER (*Monatsh. f. Chem.*, 2, 558—561).—As Lewkowitsch (this Journal 38, 33) could not obtain nitro-bodies by the action of nitric acid on fatty acids, the author thought he might be successful if he used brominated bodies.

Monobromacetic acid is but slowly attacked by strong nitric acid, with the production, apparently, of carbonic anhydride, hydrobromic acid, and water. Ethylene dibromide and nitric acid, when only very slightly warmed together, yield a black-brown oil, which continually gives off red fumes and is decomposed by water, the products being nitrous acid and hydrobromic acid; when, however, a mixture in proportions 1 of the former to 5 of the latter is heated to 60—70°, and as soon as the violent action sets in, cooled down in an ice-bath, and finally heated for several hours on a water-bath, nitrous fumes, bromine, and hydrobromic acid are evolved, and the product is monobromacetic acid. Bromisobutyric acid and nitric acid, under similar conditions, yield the above black-brown oil, which, the author suggests, may be nitrosyl bromide,  $NO.Br$ , and  $\alpha$ -hydroxyisobutyric acid.

D. A. L.

**Action of Organic Zinc-compounds on the Bromides of  $\alpha$ -Monobrominated Acids of Saturated Series.** By M. KASCHIRSKI (*Chem. Centr.*, 1881, 278—281).—This reaction appears to take place generally, as in the case of the action of zinc methide on monobromacetic bromide, thus:—(1)  $CH_2Br.COBr + 2ZnMe_2 = CH_2Br.CMe_2(OZnMe) + ZnBrMe$ ; (2)  $CH_2Br.CMe_2(OZnMe) - ZnBrMe = CHO.CHMe_2$ ; (3)  $CHO.CHMe_2 + ZnMe_2 = CHMe_2.CHMe(OZnMe)$ , and has been confirmed as regards the action of zinc methide on two of the three following  $\alpha$ -monobrominated acid bromides:—

(1.)  $\alpha$ -Bromopropionic bromide,  $CH_3.CHBr.COBr$  (b. p. 154—155°),

was obtained by the action of dry bromine on propionic bromide (b. p.  $104-106^{\circ}$ ) in sealed tubes. It is decomposed by water, yielding bromopropionic acid (b. p.  $202^{\circ}$ ), and by the action of zinc methyl in the proportion of 1 to 3, it gives a hydrocarbon boiling below  $100^{\circ}$ , condensed methylisopropyl ketone boiling below  $200^{\circ}$ , a brominated oil boiling above  $200^{\circ}$ , and *dimethylisopropyl carbinol*, the last being the chief product. This is a colourless liquid (b. p.  $118-119^{\circ}$  at 751 mm., solidifies at  $-26^{\circ}$ , sp. gr. 0.837 at  $0^{\circ}$ ). The corresponding *chloride* (b. p.  $110-112^{\circ}$ , solidifying at  $-2^{\circ}$ ) and the *iodide* (boiling at  $140-142^{\circ}$ , with partial decomposition, and solidifying at  $0^{\circ}$ ) were also obtained. The *hexylene* (b. p.  $72-74^{\circ}$  at 750 mm.) combines with bromine to form the *dibromide*  $C_6H_{12}Br_2$  (m. p.  $169-170^{\circ}$ ), which is easily soluble in alcohol, but less soluble in ether. On oxidation with chromic acid, the dimethylisopropyl carbinol (which is identical with Pawlow's alcohol) gives acetic acid together with a little acetone and hydrocarbon.

(2.)  *$\alpha$ -Bromisobutyric bromide*,  $CMe_2Br.COBr$  (b. p.  $162-164^{\circ}$ ), was obtained in an analogous manner from isobutyric bromide (b. p.  $116-118^{\circ}$ ), and converted by the action of water into  *$\alpha$ -bromisobutyric acid* (m. p.  $48^{\circ}$ ), and thence into  *$\alpha$ -hydroxyisobutyric acid* (m. p.  $80^{\circ}$ ). On treatment with zinc methide,  *$\alpha$ -bromisobutyric bromide* gives ordinary pinacolin,  $CMe_3.COMe$  (b. p.  $105-107^{\circ}$ ), and Butlerow's pentamethyl alcohol hydrate,  $2C_7H_{16}O + H_2O$ , crystallising in long needles (m. p.  $83^{\circ}$ ), and smelling strongly of camphor. The corresponding *chloride* (m. p.  $135^{\circ}$ ), *bromide* (m. p.  $150^{\circ}$ ), *iodide* (m. p.  $142^{\circ}$  with decomposition), *heptylene* (b. p.  $80^{\circ}$ ) and *heptylene dibromide*, were prepared and examined; the last is a solid easily fusible mass.

(3.)  *$\alpha$ -Bromobutyric bromide*,  $CH_2EtBr.COBr$  (b. p.  $172-174^{\circ}$ ), was obtained from butyric bromide (b. p.  $126-127^{\circ}$ ), and was further converted successively into  *$\alpha$ -bromobutyric acid* (b. p.  $214-217^{\circ}$ ) and  *$\alpha$ -hydroxybutyric acid*, an easily fusible crystalline mass. By the action of zinc-methyl  *$\alpha$ -bromobutyric bromide* gives a hydrocarbon, a brominated oil, and a heptyl alcohol, which is a thick liquid (b. p.  $138-140^{\circ}$  at 750 mm., sp. gr. 0.8487 at  $0^{\circ}$ , 0.8329 at  $21^{\circ}$ ) possessing a characteristic camphor-like odour. The corresponding *chloride* (b. p.  $135-138^{\circ}$  at 757 mm., sp. gr. 0.899 at  $0^{\circ}$ , 0.844 at  $22^{\circ}$ ) does not solidify at  $-15^{\circ}$ . The *iodide* boils with decomposition at  $145-147^{\circ}$ , and has a sp. gr. of 1.391 at  $0^{\circ}$ , and 1.373 at  $10^{\circ}$ . The *heptylene* (b. p.  $92-95^{\circ}$  at 755 mm., sp. gr. 0.7355 at  $0^{\circ}$ , and 0.7188 at  $21^{\circ}$ ) is a liquid of an odour different from that of other olefines. On oxidation with chromic acid, the alcohol gives acetone, methyl ethyl ketone (?), and on further oxidation acetic acid; it is therefore different from any of the three known heptyl alcohols, and must be either methyl-ethyl-isopropyl carbinol,  $CMeEtPr^e.OH$ , or dimethyl-pseudobutyl carbinol,  $CHMeEt.CMe_2.OH$ , the heptylene having in either case the constitution of trimethylethylethylene,  $CMe_2:CMeEt$ .

The author considers that Pawlow's (*Chem. Centr.*, 76, 770) methyl-ethyl-isopropyl carbinol (b. p.  $124-127^{\circ}$ ) and trimethylethylethylene (b. p.  $75-80^{\circ}$ ) were impure, owing to admixture with dimethylisopropyl (b. p.  $118^{\circ}$ ) and other hydrocarbons.

T. C.



**Action of Metals on Ethyl Bromopropionate.** By E. SCHERKS (*Monatsh. f. Chem.*, **2**, 541—546).—When this ethereal salt is heated with zinc-dust, violent reaction takes place, carbonic oxide is given off, and besides unattacked ether, ethyl bromide and ethyl propionate distil over. The residue consists of zinc dimethylsuccinate. Precipitated silver acts in a similar manner; there is, however, no carbonic oxide evolved.  
D. A. L.

**Derivatives of Acrylic Acid.** By P. MELIKOFF (*Chem. Centr.*, 1881, 354).—Chlorolactic acid is obtained by the action of hypochlorous acid on an aqueous solution of acrylic acid at 0°. It is a thick, almost odourless liquid, soluble in all proportions in water, alcohol, and ether, and is decomposed on heating. The *ethyl salt*,  $C_3H_5EtClO_3$ , is an oily liquid (b. p. 160—185° at 174 mm.), which is only sparingly soluble in water, but soluble in all proportions in alcohol and ether. The *barium salt*,  $(C_3H_5ClO_3)_2Ba$ , is amorphous. The free acid is easily reduced to glyceric acid by moist silver oxide, or by heating with an aqueous solution of the silver salt at 120° in sealed tubes, the reaction being analogous to that which occurs with fermentation lactic acid from  $\alpha$ -chloropropionic acid.

*Amidolactic acid* or *Isoserin*,  $C_3H_5(NH_2)O_3$ , obtained by the action of ammonia on ethylchlorolactic acid, crystallises in monoclinic prisms, which are only sparingly soluble in cold, but easily in hot water. It combines with both bases and acids, and agrees in all its properties with Cramer's serin from silk, except that it is less soluble in water; 1 part of serin dissolving in 24·2 parts, and 1 part of isoserin in about 65·4 parts of water.

Dichloropropionic acid is easily obtained by the action of hydrochloric acid, saturated at 0°, on chlorolactic acid in sealed tubes at 100°. It crystallises in needles (m. p. 50°), and is identical with the acid obtained by Henry from dichlorhydrin, and by Werigo and Melikoff from  $\beta$ -chloracrylic acid.

By the action of hypochlorous acid on acrylic acid, the formation of  $\alpha$ - or  $\beta$ -chloropropionic acid (or both) was to be expected. The chlorolactic acid described above should therefore be chlorethylenelactic acid, and should on reduction give hydracrylic acid or fermentation lactic acid respectively. Actual reduction by zinc and sulphuric acid gave propionic and hydracrylic acids; the liquid chlorolactic acid, therefore, is, or contains, chlorhydracrylic acid (*i.e.*, the  $\alpha$ -chlor-acid), but it also contains the  $\beta$ -chlor-acid, since it gives two distinct zinc salts, one of which crystallises in prisms and plates,  $(C_3H_5ClO_3)_2Zn + 3H_2O$ , whilst the other is amorphous,  $(C_3H_4ClO_3)_2Zn$ . The former salt, on decomposition with sulphuric acid, gives an acid crystallising in slender prisms (m. p. 78°), which are easily soluble in ether, alcohol, and water; it is identical with the  $\beta$ -chlorolactic acid,  $CH_2Cl.CH(OH).COOH$ , obtained by Richter, by the oxidation of epichlorhydrin, and by the author from glycidic acid by means of hydrochloric acid. The amorphous zinc salt gave  $\alpha$ -chlorolactic acid,  $CH_2(OH).CHCl.COOH$ , which by the action of hydriodic acid was converted into  $\beta$ -iodopropionic acid.  
T. C.

**Ethylic Monochloromalonate and Tartronic Acid.** By M. CONRAD and C. A. BISCHOFF (*Annalen*, **209**, 218—232).—Pure tartronic acid,  $\text{OH} \cdot \text{CH}(\text{COOH})_2$ , prepared from ethyl monochloromalonate, as previously described by the authors (*Ber.*, **13**, 600, and **14**, 617), crystallises in transparent prisms, soluble in alcohol, ether, and water. The acid sublimes at  $110$ — $120^\circ$ , and melts with decomposition at  $185$ — $187^\circ$ .  $\text{C}_3\text{H}_2\text{O}_5\text{Pb}$  is crystalline and sparingly soluble.  $\text{C}_3\text{H}_2\text{O}_5\text{K}_2$  and  $\text{C}_3\text{H}_2\text{O}_5\text{Na}_2$  are crystalline salts, sparingly soluble in alcohol.  $\text{C}_3\text{H}_2\text{O}_5\text{Ag}_2$  is deposited from a hot aqueous solution in needle-shaped crystals. A neutral solution of ammonium tartronate gives white precipitates with barium, calcium, zinc, and mercurous salts, a white crystalline precipitate with manganese sulphate, bluish-green crystalline precipitate with copper, and a red flocculent precipitate with cobalt salts. Nickel, aluminium, magnesium, and mercuric salts do not yield any precipitate with a neutral tartronate.

*Chlormalonylamide*,  $\text{CHCl}(\text{CONH}_2)_2$ , is deposited in colourless plates, when alcoholic ammonia is left in contact with ethyl monochloromalonate.

*Anilidomalonylanilide*, formed by boiling a mixture of aniline and ethyl monochloromalonate, crystallises in prisms which melt at  $162^\circ$ .

W. C. W.

**Ethylic Nitrosomalonate and its Derivatives.** By M. CONRAD and C. A. BISCHOFF (*Annalen*, **209**, 211—218).—Ethylic nitrosomalonic acid and its metallic derivatives have been previously described by the authors (*Ber.*, **13**, 595—601; this Journal, Abstr., 1880, 629). *Nitrosobenzylmalonic acid*,  $\text{C}_7\text{H}_7\text{C}(\text{NO}) \cdot (\text{COOH})_2$ , prepared by the action of hydrochloric acid on the silver salt, crystallises in plates, which melt at  $120^\circ$ , and at the same time decompose, forming hydrocyanic and carbonic acids and benzyl alcohol. The preparation of the ethyl and potassium salts of this acid have already been described (*loc. cit.*). An aqueous solution of potassium nitrosobenzylmalonate produces a sparingly soluble crystalline precipitate with silver nitrate, and a pale blue crystalline precipitate with copper sulphate solution, to which a drop of ammonia has been added.

W. C. W.

**Ethylic Salts of Ethyl- and Isobutyl-chloromalonic Acid, Ethyl- and Isobutyl-tartronic Acids, Ethyl- and Isobutyl-hydroxyacetic Acid.** By M. GUTHZEIT (*Annalen*, **209**, 232—241).—The ethylic salt of ethylchloromalonic acid,  $\text{C}_6\text{H}_5\text{Cl}(\text{COOEt})_2$ , is a colourless oil, sp. gr. 1.11 at  $17^\circ$ . On saponification with potassium hydroxide, it yields ethyltartronic acid,  $\text{OH} \cdot \text{C}_6\text{H}_5(\text{COOH})_2$ , a white crystalline mass, soluble in alcohol, ether, and water. The acid melts at  $98^\circ$ , with evolution of carbonic anhydride. By the action of heat at  $180^\circ$ , it is completely converted into hydroxybutyric acid.

*Diethylmalonic acid* is decomposed by the action of bromine and water, with formation of diethoxalic and diethylacetic acids.

*Ethylic isobutylmalonate* is soluble in alcohol and ether, but is not miscible with water. It boils at  $225^\circ$ , and has a sp. gr. of 0.983 at  $17^\circ$ .

*Isobutylmalonic acid* is a crystalline body, soluble in water, alcohol, and ether. It melts at  $107^\circ$ , with decomposition.

*Ethyl isobutylchloromalonate* is not miscible with water. It boils at  $246^{\circ}$ , and has a sp. gr. of 1.021 at  $15^{\circ}$ . On saponification with potassium hydroxide, it yields *isobutyltartronic acid*,  $\text{CH}_2\text{CBu}(\text{COOH})_2$ . This acid forms a white crystalline deliquescent mass, very soluble in ether, alcohol, and water. It melts between  $110^{\circ}$  and  $114^{\circ}$ , and yields isobutylhydroxyacetic acid, when heated at  $180^{\circ}$ . Isobutylhydroxyacetic acid crystallises in white plates (m. p.  $56^{\circ}$ ). Its zinc salt,  $(\text{C}_6\text{H}_{11}\text{O}_3)_2\text{Zn} + 2\text{H}_2\text{O}$ , crystallises in silky scales. 0.121 part of the anhydrous salt requires 100 parts of water at  $16^{\circ}$  for solution. In many of its properties this acid resembles the  $\alpha$ -hydroxyisobutylacetic acid, which has been investigated by Erlenmeyer and Sigel (*Ber.*, **7**, 1109), and by Ley (*ibid.*, **10**, 231). W. C. W.

**Isomalic Acid.** By M. SCHMOEGER (*J. pr. Chem.* [2], **24**, 38—44).—The author describes the following points of difference between his isomalic acid, already described in this Journal (**36**, 618), and Böttinger's methyltartronic acid [hydroxyethylidenesuccinic acid], described in this vol. (413), the last-mentioned author having suggested that the difference was that the author's acid formed no crystalline salts, which is not the fact.

Isomalic acid yields non-crystalline precipitates with calcium, barium, lead, and in strong solutions with silver salts; the latter is, however, precipitated in the form of flat pyramids from dilute solutions; both varieties (the amorphous and crystalline) of the silver salt, change spontaneously into needles in the presence of moisture. By dissolving the amorphous barium salt in 100 times its weight of boiling water, and evaporating the solution, the salt is obtained in tablets with parallel sides; the formula is  $\text{C}_4\text{H}_4\text{BaO}_5 + 2\text{H}_2\text{O}$ : it loses its water of crystallisation over sulphuric acid, or by drying in the air at  $130^{\circ}$ . The dry salt is hygroscopic; a sample left exposed to the air for about one hour absorbed 3 per cent. of water. The acid melts at  $140^{\circ}$ ; a 10 per cent. solution in a 100 mm. tube had no effect on the plane of polarisation; heated to about  $170^{\circ}$ , it yields carbonic anhydride and lactic acid.

By heating 5 grams of isosuccinic acid with 10 c.c. of water, and 14 grams of bromine in a sealed tube for six hours in a water-bath, dibromopropionic acid (m. p.  $58^{\circ}$ ) and carbonic anhydride are formed. D. A. L.

**Isoheptoic Acid from  $\beta$ -Hexyl Iodide.** By O. HECHT (*Annalen*, **209**, 309—338).— $\beta$ -Hexyl iodide, prepared by the action of amorphous phosphorus and hydriodic acid on mannitol, was converted into cyanide by heating with alcoholic potassium cyanide, and then into isoheptoic acid by boiling with potash. After purification, the acid has a sp. gr. at  $0^{\circ}$  of 0.9305, and becomes thick at  $-25^{\circ}$ . It is a clear oily liquid (b. p.  $211.5^{\circ}$ ) having a weak rancid odour, and is miscible in all proportions with alcohol, ether, benzene, &c., one part being soluble in 278 parts water at  $4^{\circ}$ . The sodium salt gives white precipitates, more or less sparingly soluble, with Al, Zn, Cd, Mn, Pb, Hg, and Ag salts; the calcium salt precipitates on warming. On oxidation, isoheptoic acid yields a mixture of butyric and acetic acids, which proves its constitution to be  $\text{CH}_2\text{Me}(\text{CH}_2)_2\text{CHMe.COOH}$ ,

whence it may be termed methylbutylacetic acid. The acid products of oxidation were separated by fractional distillation with water.

Methyl isoheptoate is a limpid, strongly smelling liquid (b. p. 156—157°), which does not solidify at -20°. Its sp. gr. is 0·8790 at 15°. The ethyl salt has a fruity odour, boils at 172—173°, and has a sp. gr. at 15° of 0·8685. Propyl isoheptoate, not so limpid as the foregoing, boils at 191—192°, and its sp. gr. at 19° is 0·8635, compared with water at 15°. The isopropyl ether (b. p. 177°) was not obtained quite pure. Potassium isoheptoate forms a deliquescent crystalline mass, easily soluble in water and alcohol; the sodium salt is less hygroscopic, and the lithium salt not at all. The salts of the alkaline earth metals crystallise with 1 or 2 mols.  $\text{H}_2\text{O}$ , 100 parts of water dissolving 13·8 parts of the calcium salt at 3°, 8·8 at 50°, and 6·46 at 89°. The silver salt is slightly soluble in water, and on evaporation separates in needles; it is unaltered in diffused daylight. J. K. C.

**Pyroterebic Acid.** By C. GEISLER (*Annalen*, **208**, 37—55).—It has already been shown (this Journal, **38**, 315) that the product of the dry distillation of terebic acid was a mixture containing two isomeric bodies, pyroterebic acid, and a lactone of the formula  $\text{C}_6\text{H}_{10}\text{O}_2$ ; since then a third body, *teraconic acid*, has been found.

Pyroterebic acid is obtained in largest quantities when the distillation is conducted as quickly as possible. The product is treated with water, and baryta is added until the liquid becomes alkaline; carbonic anhydride is now passed through until the barium carbonate first precipitated is redissolved; the lactone is extracted with ether; and, on evaporating down the residue to a small volume, barium teraconate crystallises out, and is collected. The barium pyroterebate which remains in the mother-liquor is decomposed; and the acid is distilled with steam and purified by its calcium salt; the yield is about 14 per cent. of the terebic acid used. *Pyroterebic acid*,  $\text{C}_6\text{H}_{10}\text{O}_2$ , does not solidify at -15°, and has a characteristic sharp odour. If water is added to the dry acid, it is completely dissolved until the volume has increased to three or four times the original; on a further addition of water the liquid separates into two layers, the upper one being the aqueous acid; a very large quantity of water is now required to produce perfect solution. This acid is lighter than water, whilst the isomeric lactone is heavier. The *calcium salt*,  $(\text{C}_6\text{H}_9\text{O}_2)_2\text{Ca} + 3\text{H}_2\text{O}$ , crystallises very easily in colourless glistening prisms, more soluble in hot than in cold water. At 100° it loses  $2\frac{1}{2}\text{H}_2\text{O}$ , and is only quite free from water at 120°. Some of this salt, left for some time over sulphuric acid in a desiccator, became greatly changed; it deliquesced in the air, gave no acid when acidified with hydrochloric acid, dissolved in water to a turbid solution, and, when dried in a vacuum, was left as an amorphous transparent mass. The *silver salt*,  $\text{C}_6\text{H}_9\text{O}_2\text{Ag}$ , is scarcely soluble in cold water, but easily in hot water; by boiling with water, it becomes discoloured, and separates in coloured leafy crystals from the hot filtered solution. By boiling with water or by distilling with steam, the acid remains unchanged. Pyroterebic acid is converted into its isomeric lactone partially on distillation, and completely by digesting at its boiling point. The action of hydrobromic acid on this acid has

already been described (this Journal, **38** 378). Bromine converts it into oily bye-products and *dibromisocaproic acid*, which crystallises from carbon bisulphide in large colourless crystals (m. p. 99–100°); cold water is without action on this, but on warming it, the acid melts at about 70°, and, on boiling, dissolves with decomposition. This decomposition takes place more readily in neutral or alkaline solutions; the product, *terelactone*,  $C_6H_8O_2$ , † b. p. 210°, is a colourless mobile liquid, which easily solidifies at low temperatures, and remelts at 10–12°. It takes four times its volume of water to dissolve it at ordinary temperatures, and is reprecipitated from this solution by potassium carbonate. With bromine, it slowly forms a liquid addition-product. By digestion with baryta, it is converted into the salt of the corresponding hydroxy-acid. On evaporating the alcoholic solution of this salt in a desiccator, it remains behind as a vitreous mass. It is very unstable; its aqueous solution deposits barium carbonate when evaporated on a water-bath, and on heating the dry salt at 100° in an air-bath it continually loses weight.

*Teraconic acid*,  $C_7H_{10}O_4$ .—The barium salt, mentioned above, is dissolved in dilute hydrochloric acid, and the acid extracted with ether, from which solution it crystallises in large, well-formed asymmetric crystals (m. p. 161–163°).\* The new acid is soluble in cold water and ether, and very soluble in boiling water and alcohol; it is dibasic, thus differing from its isomeride terebic acid.

The *barium salt*,  $C_7H_8O_4Ba$ , is precipitated in brilliant crystals when barium chloride is added to a solution of the ammonium salt, only slowly in the cold, but quickly when the solution is warmed; when once precipitated, the salt is very sparingly soluble in water; the *calcium salt*,  $C_7H_8O_4Ca$ , is precipitated as a sandy powder: in other respects, it resembles the barium salt. When teraconic acid is heated to 160°, water is eliminated and an anhydride is formed, which boils with slight decomposition at 270–280°, and recombines with water to form the acid. Hydrobromic acid converts it into terebic acid, its isomeric lactone. Ethyl terebate is converted into the teraconate by the action of sodium. Teraconic acid forms a well crystallised bromine addition-product.

D. A. L.

**Terpenylic Acid, Teracrylic Acid, and Heptalactone.** By R. FITTIG and O. KRAFFT (*Annalen*, **208**, 71–91).—Terpenylic acid mixed with terebic acid is obtained by the oxidation of turpentine-oil with potassium dichromate and sulphuric acid; they are separated by treating the mixture of acids with ether until about two-thirds is dissolved; the residue is almost pure terebic acid; the extract contains the terpenylic acid, which is further purified by repeated crystallisation from dilute aqueous solution, a crystal of terpenylic acid being used to start the crystallisation each time. If the terpenylic acid is pure, it will all melt at 70°; if, on the other hand, terebic acid is present, there will be crystals floating about in the clear liquid. Besides these two acids, acetic and terephthalic acids are formed in this reaction; the terpenes from lemon oil (b. p. 175°), carraway (b. p.

\* Crystals marked thus \* are measured by Fock. Boiling points marked thus † are taken with the mercury column entirely in the vapour.

178°), and parsley (b. p. 157·5—158°), behave in a similar manner. Terpenylic acid crystallises in asymmetric prisms.\*\* On oxidation, it breaks up into carbonic anhydride and acetic acid. Sodium amalgam is without action on it. Its salts have already been described by Hempel (*Annalen*, **180**, 71). Like terebic acid, on warming with alkaline hydroxides, it is converted into salts of a dibasic acid,  $C_8H_{14}O_5$ , which the authors call diaterpenylic acid; the *barium salt*,  $C_8H_{12}O_5Ba + 2H_2O$ , crystallises in beautiful glistening prisms, which are very hard, and stick so fast to the sides of the vessel that they can scarcely be removed. The  $2H_2O$  are driven off at 190—200°. The salt is only slightly soluble in water. The *silver salt*,  $C_8H_{12}O_5Ag_2$ , is a thick white curdy precipitate, scarcely soluble in water and only slightly discoloured by light. By decomposing these salts terpenylic acid is produced: hence this acid is also a lactonic acid.

By the dry distillation of terpenylic acid, an acid and some neutral bodies are produced; the latter have not yet been thoroughly investigated. The acid, called by the authors *teracrylic acid*,  $C_7H_{12}O_2$ , is purified by distilling it with steam, then by crystallisation as calcium salt, and finally by distillation; it boils at 218°†, and does not solidify in a freezing mixture; is colourless, has a characteristic odour resembling valeric and caproic acids, but more pleasant, is only slightly soluble in water, and is lighter than that liquid. It has no lactone mixed with it. The *calcium salt*,  $(C_7H_{11}O_2)_2Ca + 5H_2O$ , crystallises in long colourless prisms if the solution is evaporated until a skin forms on the surface, and is then allowed to evaporate spontaneously in a desiccator. Should, however, the evaporation be continued on a water-bath, a salt will separate out in white opaque masses which contain little or no water, and are redissolved on cooling and standing; if the evaporation be continued until a large quantity of the dissolved salt has thus separated out, and then left to stand some days, only part of the salt will be redissolved, and the other part will be changed into long glistening needles with  $5H_2O$ . This salt is easily soluble in cold water; if, however, it is heated with water over a free flame it loses its water of crystallisation and is precipitated as a white powder, which dissolves only in hot water. The *silver salt*,  $C_7H_{11}O_2Ag$ , forms a heavy white precipitate, crystallising from water in small white needles. It is rather unstable, is discoloured by light, and turns brown at 100°. The *barium salt* crystallises in beautiful prisms, easily soluble in water. The *potassium salt* is deliquescent in the air.

The products of the fusion of potassium teracrylate with potash are acetic acid, a small quantity of an acid which reduces silver salts, formic (?), and a non-volatile acid which is viscid, soluble in ether, only slightly in water, and as yet has not been further investigated. By the action of hydrobromic acid, teracrylic acid is first converted into a brominated acid of the formula  $C_7H_{13}BrO_6$ , and then, after five or six hours, into its isomeric lactone; this conversion is quite quantitative. *Heptolactone*,  $C_7H_{12}O_2$ , is a colourless, clear, feebly odorous liquid, solidifying at 0° to a white crystalline mass (m. p. 11°, b. p. 220°†). It is much less soluble in water than the caprolactones, requiring 12 vols. of water at 0°: its solution is equally as

\*\* Crystals marked \*\* are measured by Schimper.

sensitive as regards heat. Boiling with alkaline hydroxides converts it into the salts of *hydroxyheptylic acid*. The *barium salt*,  $(C_7H_{13}O_3)_2Ba$ , is a very hygroscopic, amorphous varnish; it is extremely soluble in water and absolute alcohol. Heated at  $100^\circ$  in an air-bath, it decomposes and constantly loses weight. The *silver salt*,  $C_7H_{13}O_3Ag$ , crystallises from its aqueous solution, after standing for some time, in druse aggregations of well formed, thick, hard, clear, colourless prisms. It is more stable than the barium salt, and does not lose weight when heated to  $80^\circ$ . Free hydroxyheptylic acid very soon breaks up into water and the lactone.

Teracrylic acid yields bromine addition-products; they cannot as yet be obtained pure on account of their instability; one is crystalline.

D. A. L.

**Products of the Dry Distillation of Terpenylic Acid.** By C. AMTHOR (*Arch. Pharm.* [3], **18**, 356—369).—To prepare terpenylic acid ( $C_8H_{12}O_4$ ) in large quantities, 100 grams of oil of turpentine are mixed with 800 of potassium dichromate, 1,000 of common sulphuric acid, and 4 litres of water, the oxidation proceeding quietly. The mixture is boiled with a reflux condenser, until it becomes green, when it is poured through a cloth to keep back the resinous products, which are washed, dried, and reserved for subsequent examination. The liquid is now evaporated to half-bulk, extracted with ether, and the ethereal solution is left at rest for two days; the clear solution poured off from the brown deposit is distilled; and the greenish residue, consisting chiefly of terpenylic, terebic, acetic, and terephthalic acids, and a syrupy acid, is diluted with water and heated, until the odour of acetic acid has disappeared. The residue is converted into sodium salts, filtered, acidified, and shaken with ether, thus leaving all the chromium, and most of the terephthalic acid behind. After distilling off the ether, diluting with water, and leaving in a cool place, most of the terebic acid crystallises out. The filtrate from it is evaporated to a smaller volume, and allowed to stand in an ice-safe as long as anything further crystallises out. The crystals separated from the mother-liquor (containing an acid mentioned by Fittig and Krafft) by pressure, are recrystallised from water, and the dry crystals are treated with an amount of ether insufficient for their complete solution, the terpenylic acid dissolving readily, but not the terebic acid. To entirely purify the terpenylic from terebic acid, the operation must be repeated some six or eight times. Some 6—7 per cent. of terpenylic acid was thus obtained from oil of turpentine. Terpenylic acid was discovered by Hempel (*Annalen*, **180**, 32). It is readily soluble in ether, alcohol, and water, at the ordinary temperature, much more sparingly in ice-cold water, from which it can be obtained in large crystals, containing 1 mol.  $H_2O$  (m. p.  $57.5$ — $58.5^\circ$ ), readily losing their water of crystallisation however, and then melting at  $89^\circ$ . Terpenylic acid must be regarded as an internal anhydride of the unknown dibasic diaterpenylic acid,  $C_8H_{14}O_6$ , similar to lactide.

In the preparation of teracrylic acid,  $C_7H_{12}O_3$ , by the dry distillation of terpenylic acid, the best yield was obtained by slowly distilling not more than 20 grams of terpenylic acid, dried as far as possible at  $40^\circ$ .

The distillate (about 40 per cent. of the terpenylic acid employed) is neutralised with potassium carbonate, separated from the undissolved oil, and the solution shaken with ether, to remove the remainder. The solution of potassium teracrylate is acidified with hydrochloric acid, and distilled by steam until the distillate is no longer acid. Teracrylic acid not being readily soluble in water, separates in the cold in drops on the surface of the liquid.

The residue in the retort is shaken up with ether several times to recover the undecomposed terpenylic acid, and after the ether is distilled off, and the residue diluted with water, it is placed aside to crystallise. A not inconsiderable amount of a syrupy brown acid remains in the mother-liquor, and cannot by any means be crystallised; it is perhaps an isomeride of teracrylic acid. Terpenylic acid appears to be dimorphous. Calcium teracrylate is readily soluble in cold and hot water, and crystallises in long needles grouped in stars. It effloresces very readily. The author confirms Krafft (*Ber.*, 10, 522).

The neutral oil obtained by the dry distillation of the terpenylic acid is dissolved by shaking with water, and poured on to a damp filter, some oily brown drops remaining undissolved; the filtered is distilled with steam, the distillate shaken with ether, and the liquid remaining, on evaporation of the latter, dried over potassium carbonate, and distilled (b. p. 202—204°, all the mercury in the vapour). By boiling 5 grams of the liquid for some hours with baryta, with a reflux condenser, removing the excess of barium by carbonic anhydride, and evaporating, a yellowish gummy mass was obtained, becoming brittle and friable on drying over sulphuric acid. The mass was recrystallised from absolute alcohol. Its composition was that of a barium hydroxyheptylate,  $\text{Ba}(\text{C}_7\text{H}_{13}\text{O}_3)_2$ . On decomposing this salt with sulphuric acid, extracting with ether and distilling the ethereal solution, a liquid was again obtained (b. p. 202—204°), of the composition  $\text{C}_7\text{H}_{12}\text{O}_2$ , therefore a lactone. Its sp. gr. at 4° is 0.9818, it is colourless, with a peculiar ethereal odour, readily inflammable, easily soluble in alcohol, ether, and water, does not solidify at  $-16^\circ$ , merely becoming thick. Potassium carbonate separates it from its aqueous solutions.

The barium salt was obtained by neutralisation. The silver salt, by decomposing the barium salt with silver nitrate. The zinc salt from zinc sulphate and the barium salt. The hydroxyheptylic acid could not be obtained in the free state.

By oxidising the lactone with warm dilute nitric acid, it yielded oxalic, but no succinic acid.

The brown drops of oil mentioned above as insoluble in water, were washed thoroughly and then dried with potassium carbonate and distilled. It boiled irregularly and above the boiling point of the lactone. On boiling it with a saturated solution of baryta in a reflux apparatus, and treating it with carbonic anhydride, &c., as above, a lactone,  $\text{C}_7\text{H}_{12}\text{O}_2$ , was obtained (b. p. 210—212°), differing from the previously described lactone by being insoluble, or but very slightly soluble in water. The silver salt was obtained as a flocculent white precipitate.

To obtain teracrylic acid, the calcium teracrylate obtained above was dissolved in a little water, decomposed by hydrochloric acid and



placed in an ice-safe. The separated acid was mechanically removed, and the remainder extracted by ether. Teracrylic acid thus obtained is a thickish oily liquid (b. p. 217—218°), dissolving in water with difficulty, but readily in alcohol and ether. The distilled acid was reconverted to the calcium salt; ether could extract nothing from this solution, no lactone having been produced. From the different behaviour of the calcium salt of the distilled from the undistilled acid, the author concludes that by distillation, teracrylic acid is converted into an isomeride, as angelic is changed into tiglic acid under the same circumstances. This acid seems also to be changed into an isomeride by one hour's boiling. The calcium salt is not very stable, being decomposed slightly on boiling.

*Ethyl teracrylate* is a colourless, highly mobile liquid (b. p. 189—191°), with a pleasant fruity odour.

By the action of hydrochloric acid a lactone boiling at 202—204° is obtained.

By the action of bromine in carbon bisulphide a bromolactone,  $C_7H_{11}BrO_2$ , and not an addition-product, is obtained. F. L. T.

**Action of Amylene Hydrochloride and of Amylene on Benzene in presence of Aluminium Chloride.** By J. ESSNER (*Bull. Soc. Chim.* [2], 36, 212—215).—When 20 grams aluminium chloride are gradually added to a slightly warmed mixture of 20 grams amylene hydrochloride and 110 grams benzene, a violent reaction takes place with evolution of hydrochloric acid. The liquid is then poured into water, and the oily layer which separates out yields amylbenzene on distillation; this is formed in greater quantity if the reaction takes place in the cold. This amylbenzene (b. p. 185—190°, sp. gr. at 0° = 0.8728), gives a bromide which remains liquid at 0°, and dissolves completely in cold alcohol. It appears to be identical with the amylbenzene obtained by Friedel and Crafts from inactive amyl chloride. It seems probable that the action of aluminium chloride and benzene on amyl chloride, would give rise to the formation of amylene and hydrochloric acid, which would combine, forming tertiary amyl chloride, the latter then reacting on the benzene: 50 grams amylene, b. p. 30—55°, when added to a mixture of 175 grams benzene and 25 grams aluminium chloride, gives rise to a violent reaction with development of much heat. Amongst the products is amylbenzene, identical with that obtained by the previous reaction. It is probably tertiary amylbenzene or dimethyl-ethyl-phenyl-methane, isomeric with the amylbenzene which Fittig and Tollens obtained by the action of sodium on bromopentane and bromobenzene, and with that obtained by Lippmann and Louguinine on treating benzylene chloride with zinc-ethyl. When propyl bromide is boiled for some time with aluminium chloride, it is converted into isopropyl bromide. Very probably amyl chloride undergoes a similar transformation by the action of aluminium chloride in presence of benzene, although the action of the aluminium chloride alone gives rise to saturated compounds. C. H. B.

**Action of Sulphuric Acid on Mono- Di- and Tri-Bromobenzene.** By J. HERZIG (*Monatsh. Chem.*, 1881, 192—199).—Mono-

bromobenzene, when heated with sulphuric acid for some hours in a vessel provided with a reflux condenser, yields dibromobenzenesulphonic acid [1 : 3 : 5], together with a small quantity of monobromobenzenedisulphonic acid. Dibromobenzene [1 : 4], similarly treated, gives a mixture of tetrabromobenzene [1 : 2 : 4 : 5] and hexabromobenzene, no sulphonic acid being formed; this is in accordance with their known instability at high temperatures. Tribromobenzene [1 : 3 : 5] gives a large yield of hexabromobenzene. As carbonic anhydride is evolved in these reactions, it appears that a portion of the bromobenzene is oxidised, its bromine then reacting on the other portion to form more highly brominated products. A. J. G.

**Preparation of Metatoluidine.** By O. WIDMANN (*Bull. Chim. Soc.* [2] **36**, 216).—Nitrobenzyl chloride,  $C_6H_4(NO_2).CHCl_2$ , is dissolved in alcohol, mixed with a considerable quantity of hydrochloric acid, cooled to  $10^\circ$ , and zinc-dust added, care being taken that the temperature does not rise above  $12^\circ$ . When all the chloride is dissolved and the liquid is no longer rendered turbid by addition of water, the liquid is heated. If these directions are attended to nothing but metatoluidine is obtained. If, however, the liquid is heated before all the chloride is reduced (which often requires several days) then a resinous substance containing chlorine is formed, as Vienne and Steiner have observed. C. H. B.

**Direct Conversion of the Aromatic Amides into their Corresponding Azo-Compounds.** By A. R. LEEDS (*Chem. News*, **44**, 210).—By the action of hydrogen peroxide on benzene, phenoloxalic acid and a small quantity of a yellow colouring matter are formed. Phenol itself is but slightly acted on by hydrogen peroxide in the cold; at the boiling heat, a tarry substance is formed. Naphthalene produces small quantities of naphthol, whilst naphthol behaves like phenol. Anthracene in glacial acetic acid solution is oxidised slowly to anthraquinone. These results show that in certain cases hydrogen peroxide acts on organic bodies by the substitution of hydroxyl, in others by direct oxidation, and in the third place by both actions combined. The experiments were therefore extended to the aromatic amides, in the hope that hydroxylated derivatives of these compounds might be obtained. The amide was converted into the acetate, or when this was not possible, it was dissolved in excess of glacial acetic acid and a solution of hydrogen peroxide, containing 1 to 2 per cent., added in successive portions.

Diphenylamine yielded a large amount of a black liquid and a black tar. Dimethylaniline, a dark red liquid with a black residue, soluble in alcohol. Xylidine, a claret-coloured liquid with a blackish residue, soluble in alcohol, forming dark purple solution. Naphthylamine gave a rose-coloured liquid with a brownish-black residue. Orthotoluidine gave a ruby-coloured liquid and a black tarry residue, soluble in alcohol. Aniline and paratoluidine acted differently. Their acetates, on gentle warming, gave a copious precipitate of a brownish crystalline appearance, which, when dried and sublimed, formed, in the case of paratoluidine, yellow needles; these were repeatedly

crystallised from alcohol, and finally gave magnificent orange needles of parazotoluene, m. p. 143—144°. The sublimate from the aniline product yielded large red crystals, together with some accompanying yellow oil. It had a melting point of 66°, showing that the body was azobenzene.

D. B.

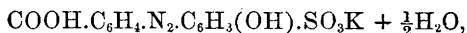
**A New Azobenzenedisulphonic Acid.** By J. V. JANOVSKY (*Monatsh. Chem.*, 1881, 219—223).—The only acid previously obtained by the direct action of pyrosulphuric acid on azobenzene is the monosulphonic acid described by Griess (*Annalen*, **131**, 89).

When the liquid from which this acid has crystallised is further evaporated, first on a water-bath, afterwards in a vacuum, it yields the new disulphonic acid. A better yield is obtained by heating azobenzene with 5 parts of crystallised pyrosulphuric acid at 150° for about 30—40 minutes; no monosulphonic acid is then formed, and after dilution with three parts of water and evaporation in a vacuum, the acid crystallises in deliquescent orange-red needles of the rhombic system, showing the combination  $\infty P\infty$ ,  $\infty \bar{P}\infty$  and  $\bar{P}\infty$ , and having the formula  $C_{12}H_8N_2(SO_3H)_2 \cdot 2H_2O$ . The *potassium* salt crystallises with  $3H_2O$  in orange-coloured rhombic prisms; the *silver* salt when crystallised from boiling water, forms anhydrous microscopic needles; the *barium* salt is sparingly soluble even in boiling water, the calcium and lead salts being more soluble. A comparison of the reactions of this acid with those of the symmetric acids prepared by reduction from the nitrobenzenedisulphonic acids, shows no agreement. Some indications were obtained of the existence of another acid in the mother-liquor.

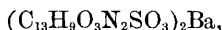
A. J. G.

**Diazo-Compounds.** PART VII. By P. GRIESS (*Ber.*, **14**, 2032—2042).—*Metazoxybenzophenol*,  $C_6H_4(COOH) \cdot N : N \cdot C_6H_4 \cdot OH$ , is formed when the nitrate or hydrochloride of metadiazobenzoic acid is poured into a solution of phenol in an excess of potassium hydroxide. On adding hydrochloric acid to the alkaline liquid, the new acid is deposited in needles or plates of a red colour. The crystals melt at 220°, and decompose at a higher temperature. They are soluble in ether and alcohol. The *barium* salt,  $(OH \cdot C_6H_4 \cdot N : N \cdot C_6H_4 \cdot COO)_2Ba + 3\frac{1}{2}H_2O$ , is deposited from a hot aqueous solution in pale yellow needles, soluble in alcohol.

*Potassium metazoxybenzorthosulphonate*,



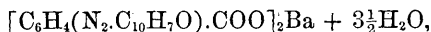
formed by the action of an alkaline solution of potassium orthophenol-sulphonate on metadiazobenzoic nitrate, crystallises in four-sided plates or prisms of a yellow colour. The free acid is precipitated in brownish-red crystalline granules, when strong hydrochloric acid is added to a hot aqueous solution of this potassium salt. The acid is soluble in water, alcohol, and ether. It forms two barium salts, viz. :



crystallising in pale yellow needles or scales, and  $C_{13}H_8O_3N_2SO_3Ba + H_2O$ , in dark yellow crystals.

*Metazoxybenzoyl-resorcinol*,  $\text{COOH.C}_6\text{H}_4.\text{N}_2.\text{C}_6\text{H}_3(\text{OH})_2$ , crystallises in brown plates or needles soluble in alcohol. This acid detonates when heated. Its solutions dye wool and silk yellow.

*Metazoxybenzoyl-β-naphthol*,  $\text{COOH.C}_6\text{H}_4.\text{N}_2.\text{C}_{10}\text{H}_6.\text{OH}$ , forms red needles or plates (m. p.  $235^\circ$ ) soluble in boiling alcohol. The potassium salt,  $\text{C}_6\text{H}_4(\text{N}_2.\text{C}_{10}\text{H}_7\text{O}).\text{COOK} + 2\text{H}_2\text{O}$ , crystallises in small needles or plates of a reddish-yellow colour. The *barium salt*,

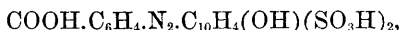


is a scarlet powder. The *ethyl salt* forms six-sided plates (m. p.  $104^\circ$ ) soluble in ether.

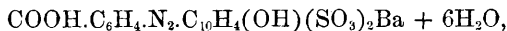
The amide is formed when an alkaline solution of  $\beta$ -naphthol acts on diazobenzamide nitrate. From boiling alcohol, in which it is only slightly soluble, the amide is deposited in slender needles of an orange colour.

*Metazoxybenzoyl-β-naphtholsulphonic acid* forms dark brown needles or plates having a green lustre. It is sparingly soluble in hot water and alcohol. It dyes wool and silk orange. The barium salt,  $(\text{COOH.C}_6\text{H}_4.\text{N}_2.\text{C}_{10}\text{H}_6.\text{O.SO}_3)_2\text{Ba} + 4\text{H}_2\text{O}$ , crystallises in slender needles of a reddish-yellow colour.

To prepare *metazoxybenzoyl-β-naphthol-α-disulphonic acid*,

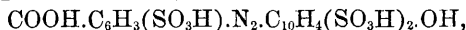


an aqueous solution of sodium  $\beta$ -naphthol- $\alpha$ -disulphonate is mixed with ammonia and diazoxybenzoyl-nitrate. After some time, the liquid is diluted, acidified with hydrochloric acid, and mixed with a boiling solution of barium chloride. The red amorphous precipitate, which consists of the acid barium salt,



is filtered, washed, suspended in water, and decomposed by the theoretical quantity of sulphuric acid. On evaporating the filtrate from the precipitated barium sulphate, the new acid remains as a yellowish-red semicrystalline mass. It is soluble in water and alcohol, and is precipitated from its alcoholic solution by the addition of ether. The neutral barium salt,  $[\text{COO.C}_6\text{H}_4.\text{N}_2.\text{C}_{10}\text{H}_4(\text{OH})(\text{SO}_3)_2]_2\text{Ba}_3 + 12\text{H}_2\text{O}$ , is a red crystalline powder.

*Metazoxysulphobenzoyl-β-naphthol-α-disulphonic acid*,

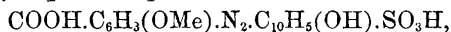


crystallises in yellowish-red needles or prisms, soluble in water and alcohol. The acid barium salt forms yellow needles sparingly soluble in hot water; the neutral barium salt forms red crystals insoluble in water.

*Azoxyanisyl-β-naphthol*,  $\text{COOH.C}_6\text{H}_3(\text{OMe}).\text{N}_2.\text{C}_{10}\text{H}_6.\text{OH} + 1\frac{1}{2}\text{H}_2\text{O}$ , is sparingly soluble in alcohol, ether, benzene, and chloroform.

$[\text{C}_6\text{H}_3(\text{N}_2.\text{C}_{10}\text{H}_6.\text{OH})(\text{OMe}).\text{COO}]_2\text{Ba} + 4\frac{1}{2}\text{H}_2\text{O}$  forms small red needles.

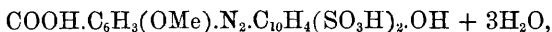
*Azoxyanisyl-β-naphthol sulphonic acid*,



crystallises in dark-red needles, soluble in alcohol and in pure water.

Wool and silk are dyed scarlet by this acid. The acid barium salt forms dark-red needles containing 8 mols.  $\text{H}_2\text{O}$ .

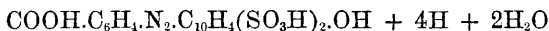
*Azoxyanisyl- $\beta$ -naphthol- $\alpha$ -disulphonic acid,*



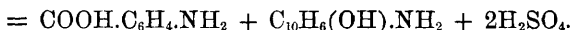
resembles the preceding acid in appearance.

*$\beta$ -Naphtholazohippuric acid,*  $\text{COOH.CH.NH.CO.C}_6\text{H}_4.\text{N}_2.\text{C}_{10}\text{H}_6.\text{OH}$ , is deposited from its alcoholic solution in reddish-yellow needles, which decompose when heated to the melting point.

All those compounds which contain  $\text{SO}_3\text{H}$  in the naphthol-group, split up on reduction with tin and hydrochloric acid, with formation of free sulphuric acid :



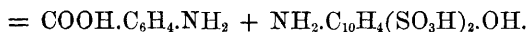
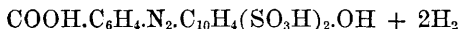
*Azobenzoic  $\beta$ -naphthol- $\alpha$ -disulphonic acid.*



*Amidobenzoic acid.*

*$\beta$ -amidonaphthol.*

If ammonium sulphide is used as the reducing agent, no sulphuric acid is liberated :



*$\beta$ -amidonaphthol- $\alpha$ -disulphonic acid.*

This disulphonic acid crystallises in dirty-white scales, containing 3 mols.  $\text{H}_2\text{O}$ , soluble in water and alcohol. The corresponding monosulphonic acid forms grey needles or prisms, sparingly soluble in hot water, hydrochloric acid, and alcohol. W. C. W.

**Phenylsarcosine.** By F. TIEMANN and R. PRIEST (*Ber.*, **14**, 1982—1984).—When benzaldehyde cyanhydrin is digested in a closed flask for five hours with an alcoholic solution of methylamine at  $70^\circ$ , phenylsarcosine nitril is formed. To separate this body from benzaldehyde, the crude product is dissolved in hydrochloric acid and filtered. The filtrate is mixed with potash and extracted with ether. The nitril in the solution is converted into the hydrochloride of phenylsarcosinamide,  $\text{CHPh.NHMe.CONH}_2.\text{HCl}$ , by the action of strong hydrochloric acid. The hydrochloride and the free amide crystallise in needles. On boiling with dilute hydrochloric acid, the amide is slowly converted into phenylsarcosine hydrochloride, which crystallises in plates soluble in alcohol and in water. *Phenylsarcosine*,  $\text{CHPh.NHMe.COOH}$ , forms slender plates insoluble in alcohol and ether. It sublimes at  $274^\circ$  without melting.

Aniline unites with the cyanhydrins of aldehydes and ketones, forming crystalline compounds. W. C. W.

**Constituents of Wood Tar.** By F. TIEMANN and P. KOPPE (*Ber.*, **14**, 2005—2014).—The acid wood tar oils boiling between  $180^\circ$  and  $300^\circ$  contain phenol, paracresol,  $\alpha$ -metaxyleneol, guaiacol, creosol, and the dimethylic ethers of pyrogallol, methylpyrogallol, and propyl-

pyrogallol. The constituents may be separated into three different classes, viz., indifferent, cresol, and guaiacol oils, by the following treatment. A solution of oil in double its volume of ether is shaken with 5 per cent. potash-solution, the acid oils are taken up by the alkali, and the indifferent oils remain in the ether. The alkaline solution is acidified with sulphuric acid and extracted with ether. After evaporating the ether, the residue is distilled and the distillate is mixed with half its volume of ether and twice its volume of a saturated solution of alcoholic potash. The guaiacol and cresol are deposited as a crystalline potassium compound; the filtrate contains cresol and its homologues.

W. C. W.

**Two New Nitrophenols.** By F. FITTICA (*J. pr. Chem.* [2], **24**, 1—15; comp. Abstr., 1881, 46).—This paper is an answer to Natanson (*ibid.*, **38**, 463) and Claus (*ibid.*, 647), and a further support to the hypothesis suggested by the author in a former paper (*ibid.*, **36**, 150—153).

*Fourth Mononitrophenol* (m. p. 31°; b. p. 205—207°).—If a mixture of this modification and orthonitrophenol is heated at 31—34°, the former will melt whilst the latter remains unfused until the temperature rises to 45°. On cooling, the ortho-derivative separates out at first, the fourth derivative remaining liquid and solidifying later on.

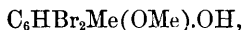
In making fourth amidophenol by the reduction of the nitrophenol with tin and hydrochloric acid, it is necessary to have the metal in excess, and to prevent the temperature from rising too high; for otherwise the product will be orthoamidophenol. The sulphate of fourth amidophenol melts at 220° with decomposition.

By treating fifth nitrophenol very carefully with tin and hydrochloric acid, the author obtains a molecular compound of the nitrophenol with hydrochloric acid,  $(\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_3\text{HCl}$ , crystallising from water in needles (m. p. 110°); on decomposing with sodium carbonate it reproduces the nitrophenol (m. p. 108°). He, therefore, thinks that the production of the fifth amidophenol mentioned in the paper referred to above depends upon some special condition with which he himself is not yet acquainted.

D. A. L.

**Constitution of Orcinol.** By F. TIEMANN and F. STRENG (*Ber.*, **14**, 1999—2005).—To prepare *dimethylorcinol*,  $\text{C}_6\text{H}_3\text{Me}(\text{OMe})_2$ , a mixture of anhydrous orcinol (1 part), potash (1 part), methyl iodide (3 parts), and methyl alcohol is boiled for six hours in a flask fitted with an upright condenser. After the addition of water, the product is evaporated to expel the methyl alcohol, and the residue is acidified with sulphuric acid and extracted with ether. The ethereal solution is shaken with a 5 per cent. solution of potash, which dissolves orcinol and monomethylorcinol, but leaves dimethylorcinol in the ether. On evaporating the ether, dimethylorcinol remains as a pale yellow liquid (b. p. 244°), miscible with alcohol, ether, and benzene. When bromine-water is added to the alcoholic solution of dimethylorcinol, *dibromodimethylorcinol*,  $\text{C}_6\text{HBr}_2\text{Me}(\text{OMe})_2$ , is obtained. This substance crystallises in colourless plates (m. p. 160°), soluble in alcohol, ether, and benzene.

To extract the *monomethylorcinol* from the dilute potash solution mentioned above, the liquid is acidified with sulphuric acid and treated with ether. After evaporating the ethereal solution, the residue is washed with water to remove orcinol, and distilled. Monomethylorcinol is a syrupy liquid (b. p. 273°), soluble in ether, alcohol, and benzene. Dibromomonomethylorcinol,



crystallises in white needles (m. p. 146°).

On oxidation with potassium permanganate, dimethylresorcinol yields an acid, which is identical with dimethyl- $\alpha$ -resorcylic acid, prepared by saponifying the methyl salt obtained by the action of potash and methyl iodide on  $\alpha$ -resorcylic acid.

*Dimethyl- $\alpha$ -resorcylic acid*,  $\text{C}_6\text{H}_3(\text{OMe})_2\text{COOH}$  [3 : 5 : 1] crystallises in needles (m. p. 176°), soluble in alcohol, ether, and hot water. The salts of the alkalis and alkaline earths are soluble. Ammonium dimethyl- $\alpha$ -resorcyate gives crystalline precipitates, with silver, lead, zinc, and copper salts. The formation of this acid from orcinol proves that the latter has the constitution ascribed to it by Vogt and Henninger (*Ber.*, 5, 326), viz.,  $\text{C}_6\text{H}_3\text{Me}(\text{OH})_2$  [1 : 3 : 5].

W. C. W.

**Quinol Derivatives.** By F. TIEMANN and W. H. MAX MÜLLER (*Ber.*, 14, 1985—1999).—Gentisic acid, also known as hydroxysalicylic or quinolcarboxylic acid, has been described by Lautemann (*Annalen*, 118, 372; 120, 311); Liechti (*Ann. Supp.*, 7, 144); Demole (*Ber.*, 7, 1436); and by von Rakowski and Leppert (*Ber.*, 8, 788). *Gentisic aldehyde*,  $\text{C}_6\text{H}_3(\text{COH})(\text{OH})_2$  [1 : 1 : 5], is prepared by heating quinol (10 grams), chloroform (100 grams), with an 18 per cent. soda solution (550 c.c.), on a water-bath for seven hours. The product is acidified with sulphuric acid, and filtered when cold. The filtrate is extracted with ether, and after the greater part of the ether has been distilled off, the remainder is treated with a solution of hydrogen sodium sulphite. The sulphite solution is decomposed by sulphuric acid, and shaken with ether. On evaporating the ethereal solution, crude gentisic aldehyde is deposited. To completely remove the quinol with which it is mixed, it is again converted into the sodium sulphite compound, which is repeatedly extracted with ether.

The pure aldehyde crystallises in lustrous yellow needles (m. p. 99°), soluble in water, alcohol, ether, chloroform, and benzene. The aqueous solution is coloured yellow by alkalis, and blue by ferric chloride. An alcoholic solution of the aldehyde unites with aniline to form a compound crystallising in beautiful red crystals. Fusion with potash converts gentisic aldehyde into gentisic acid (m. p. 196—197°).

*Monomethylquinol* (m. p. 53°) is best prepared by Rakowski's method, viz., by digesting quinol (50 parts) with potash (25·5) and methyl iodide (64·5 parts). On treating this compound with chloroform and a solution of an alkali, *metamethoxysalicylaldehyde*,  $\text{C}_6\text{H}_3(\text{COH})(\text{OH})\cdot\text{OMe}$  [1 : 2 : 5], is formed. It is volatile in a current of steam, and is purified by conversion into the hydrogen sodium sulphite compound. The aldehyde melts at + 4°, and boils at 248°; it

is soluble in alcohol and ether, and is coloured yellow by alkalis, and bluish-green by ferric chloride. By the action of hydrochloric acid in sealed tubes at  $150^{\circ}$ , it is decomposed into methyl chloride and gentisic aldehyde. An alcoholic solution of the aldehyde unites with aniline to form the compound  $C_6H_3(CHNPh)(OH).OMe$ , which crystallises in red needles (m. p.  $59^{\circ}$ ).

*Dimethylgentisic aldehyde*,  $C_6H_3(COH)(OMe)_2$  [1 : 2 : 5], is prepared by warming the sodium compound of metamethoxysalicylaldehyde, dissolved in methyl alcohol, with methyl iodide. The alcohol is distilled off, and the residue distilled in a current of steam. This substance forms slender needle-shaped crystals, soluble in alcohol, ether, and hot water. It melts at  $51^{\circ}$ , and boils at  $270^{\circ}$ ; the corresponding metaethoxysalicylaldehyde, melts at  $60^{\circ}$ , and boils at  $280-285^{\circ}$ . On oxidation with potassium permanganate, dimethylgentisic aldehyde yields, *dimethylgentisic acid*,  $C_6H_3(COOH)(OMe)_2$  [1 : 2 : 5], which crystallises in silky needles (m. p.  $76^{\circ}$ ), soluble in alcohol, ether, and hot water. The crystalline copper salt of this acid is insoluble in water. The lead salt crystallising in prisms, and the silver salt in needles, are soluble in hot water.

By the action of acetic anhydride on an ethereal solution of the sodium compound of metamethoxysalicylaldehyde, the *acetic* derivative is produced. This body forms delicate white needles (m. p.  $63^{\circ}$ ), soluble in ether, alcohol, and hot water. On oxidation with potassium permanganate it yields acetometamethoxysalicylic acid. Acetometamethoxysalicylaldehyde crystallises in needles, which melt at  $69^{\circ}$ .

On boiling metamethoxysalicylaldehyde with an excess of acetic anhydride, the compound  $C_6H_3[CH(OAc)_2](OAc).OMe$  [1 : 2 : 5], is obtained. It crystallises in needles (m. p.  $70^{\circ}$ ), soluble in alcohol, chloroform, ether, and benzene. With strong sulphuric acid, an orange coloration is produced. If the aldehyde is digested with sodium acetate

and acetic anhydride, *metamethoxycoumarin*,  $MeO.C_6H_3 \begin{array}{l} \text{CH:CH} \\ | \\ \text{O}-\text{CO} \end{array}$ , is produced. This body crystallises in plates (m. p.  $103^{\circ}$ ), freely soluble in alcohol and ether, and sparingly soluble in hot water. It is isomeric with methyl umbelliferon (*Ber.*, **12**, 996).

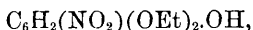
*Metamethoxysalicylic acid*,  $C_6H_3(COOH)(OH).OMe$  [1 : 2 : 5] (m. p.  $142^{\circ}$ ), prepared by heating the crude acetic derivative with an alkali, has been described by Körner and Bertoni (*Ber.*, **14**, 848).

W. C. W.

**Action of Nitrous Acid on the Ethyl Pyrogallates** By P. WESELSKY and R. BENEDIKT (*Monatsh. Chem.*, 1881, 212—218).—Monethyl pyrogallate, when treated in ethereal solution with Weselsky's reagent, yields only one well characterised product, *ethyl nitropyrogallate*,  $C_6H_3(NO_2)(OH)_2.OEt + H_2O$ , in the form of yellow plates or flat needles, of golden lustre and steel-blue shimmer. On standing over sulphuric acid, it loses its water of crystallisation, and becomes of a red-brown colour. It then melts at  $139^{\circ}$ , can be distilled by careful heating, and dissolves in alkalis with a fine red colour. Diethyl pyrogallate similarly treated yields, after several hours, long flexible, dark needles, of the formula  $C_{26}H_{25}NO_9$ . These are decom-



posed by water into nitric acid, and a white crystalline precipitate, which has all the properties of Hofmann's *ethyl-cedriret*. The mother-liquor from these crystals contains *diethyl nitropyrogallate*,



crystallising in white needles, which melt at  $123^\circ$ , dissolve in alkalis with yellow colour, and can be distilled.

The action of nitrous acid on triethyl pyrogallate gives no noteworthy result, but by the action of nitric acid on a solution in glacial acetic acid, *triethyl dinitro-pyrogallate*,  $\text{C}_6\text{H}(\text{NO}_2)_2(\text{OEt})_3$ , is obtained in brilliant yellow needles (m. p.  $75^\circ$ ). Strong nitric acid, when acting on triethyl pyrogallate or its dinitro-derivative, gives a violent reaction, in which a small quantity of *triethyl trinitropyrogallate*,  $\text{C}_6(\text{NO}_2)_3(\text{OEt})_3$ , is formed. It crystallises in pale yellow needles (m. p. about  $93^\circ$ ).

A. J. G.

**Preparation of Protocatechuic Aldehyde from Catechol. Derivatives of Guaiacol and Creosol.** By F. TIEMANN and P. KOPPE (*Ber.*, **14**, 2015—2028).—*Protocatechuic aldehyde*,



(m. p.  $50^\circ$ ), can be prepared by boiling a mixture of catechol (10 parts), chloroform (100), and a 16 per cent. soda-lye (600 parts) for six hours. The product is acidified with hydrochloric acid and allowed to cool. It is then filtered, and the filtrate extracted with ether. The aldehyde in the ethereal solution is purified in the usual way by converting it into the crystalline double compound with sodium sulphite. The properties of protocatechuic aldehyde and of guaiacol have been previously described (*Ann.* **159**, 148; *Ber.*, **8**, 1123). An energetic reaction takes place when alcoholic solutions of bromine and guaiacol are mixed, a tribromo-derivative,  $\text{C}_6\text{HBr}_3(\text{OMe})(\text{OH}) [1 : 2]$  being formed. This substance crystallises in silky needles (m. p.  $102^\circ$ ), easily soluble in alcohol, ether, benzene, light petroleum, and glacial acetic acid.

*Methylguaiacol* or *dimethylcatechol*,  $\text{C}_6\text{H}_4(\text{OMe})_2$ , formed by the action of methyl iodide on a solution of guaiacol in dilute soda, is a strongly refractive liquid (b. p.  $205^\circ$ ). It is attacked by bromine-water in an alcoholic solution, yielding a dibromo-product, which crystallises in colourless prisms (m. p.  $93^\circ$ ), soluble in alcohol, ether, benzene, and light petroleum.

*Ethylguaiacol* or *ethylmethylcatechol*,  $\text{C}_6\text{H}_4(\text{OMe}).\text{OEt}$ , is a highly refractive liquid, boiling at  $213^\circ$ .

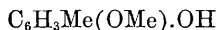
On shaking together an aqueous solution of potassium-guaiacol with potassium hydroxide and pyrosulphate, *guaiacol-potassium sulphate*,  $\text{C}_6\text{H}_4(\text{OMe}).\text{O} \cdot \text{SO}_3\text{K}$ , is deposited. This substance is precipitated on adding ether to its alcoholic solution in fine needles.

*Potassium guaiacolsulphonate*,  $\text{C}_6\text{H}_3(\text{OMe})(\text{OH}).\text{SO}_3\text{K}$ , is obtained by heating guaiacol with strong sulphuric acid. The product is poured into water, neutralised with barium carbonate, and filtered. Potassium sulphate is added to the filtrate until the barium is exactly precipitated. Two potassium salts appear to be formed, one is soluble in

alcohol and uncrystallisable; the second salt crystallises in prisms, insoluble in absolute alcohol. Attempts to replace the  $\text{SO}_3$  in these salts by cyanogen or carboxyl have been unsuccessful.

*Acetoguaiacol*,  $\text{C}_6\text{H}_4(\text{OMe})\cdot\text{OAc}$ , is a clear liquid, b. p. 235—240°.

*Vanillin* and  $\beta$ -*metamethoxysalicylaldehyde*,  $\text{C}_6\text{H}_3(\text{COH})(\text{OH})\cdot\text{OMe}$  [1 : 2 : 3], are formed on boiling guaiacol (5 grams) with soda (36), chloroform (40), and water 600 c.c. The product is acidified, exhausted with ether, and the ethereal solution treated with hydrogen sodium sulphite. The crystalline compound obtained in this way is decomposed by an acid, and on distilling the mixture of vanillin and  $\beta$ -metamethoxysalicylaldehyde in a current of steam under  $1\frac{1}{2}$  to 2 atmospheres pressure, the latter compound is carried over, and is extracted from the distillate with ether. On evaporating the ether, a yellow oil remains, which boils at 264—268°. It is soluble in alcohol, ether, chloroform, and benzene. The properties of creosol,



(b. p. 220—224°), and methylcreosol,  $\text{C}_6\text{H}_3\text{Me}(\text{OMe})_2$  (b. p. 214—218°), have been already described (*Ber.*, 10, 206, and 8, 1136).

*Metahomo- $\beta$ -metamethoxysalicylaldehyde*,  $\text{C}_6\text{H}_2(\text{COH})(\text{OH})(\text{OMe})\text{Me}$  [1 : 2 : 3 : 5], obtained by the action of chloroform on a solution of creosol in dilute soda, is an oily liquid, which boils at 270—275°. It is soluble in alcohol and ether, and ferric chloride produces an intense green coloration in its alcoholic solution. W. C. W.

**Preparation of Amido-acids from the Cyanhydrins of Aldehydes and Ketones.** By F. TIEMANN (*Ber.*, 14, 1957—1966).—The cyanhydrins are prepared by digesting the aldehydes or ketones with the equivalent quantity of aqueous hydrocyanic acid (20—30 per cent.). The mixture is slowly heated in soda-water bottles: in the case of the aromatic compounds, it is necessary to maintain the temperature at 100° for several hours. These bodies may also be prepared by the method used by Urech (*Annalen*, 164, 255) and Spiegel (*Ber.*, 14, 235, this vol., 277). The cyanhydrins of the aldehydes and ketones readily exchange their hydroxyl for  $\text{NH}_2$ , when they are treated with an equivalent quantity of alcoholic ammonia. When the reaction does not take place at the ordinary temperature, the mixture is heated in sealed tubes at 100°. The alcoholic solution is mixed with strong hydrochloric acid, and is then saponified by boiling with dilute hydrochloric acid. The alcohol and the excess of hydrochloric acid are distilled off, and the amido-acid is precipitated by ammonia, if it is insoluble in water. In the case of soluble amido-acids, the acid solution is evaporated to dryness, and the residue extracted with alcohol. The extract is evaporated and the hydrochloride of the amido-acid separated from ammonium chloride, by treatment with alcohol. To obtain the free acid, the hydrochloride is digested with oxide of silver, and the silver in the solution is removed by sulphuretted hydrogen.

The amido-acids from the aldehydes may be represented by  $\text{COOH}\cdot\text{CHR}\cdot\text{NH}_2$ , and those from the ketones by  $\text{COOH}\cdot\text{CR}_2\cdot\text{NH}_2$ .

W. C. W.

**Amido-acids from the Cyanhydrins of Benzaldehyde, Acetone, and Diethylketone.** By F. TIEMANN and L. FRIEDLÄNDER (*Ber.*, **14**, 1967—1976).—*Benzaldehyde cyanhydrin*,  $\text{CHPh}(\text{OH})\cdot\text{CN}$ , is a yellow oil, which solidifies at  $-10^\circ$ , and decomposes when strongly heated. When left in contact with strong hydrochloric acid, it forms the amide of mandelic acid,  $\text{CHPh}(\text{OH})\cdot\text{CONH}_2$ , which crystallises in white slender prisms (m. p.  $190^\circ$ ), soluble in alcohol and in hot water. It is converted into mandelic acid by boiling with hydrochloric acid.

*Phenylamido-aceto-nitril*,  $\text{CHPh}\cdot\text{NH}_2\cdot\text{CN}$ , formed by the action of alcoholic ammonia on benzaldehyde cyanhydrin, is an unstable compound. On evaporating a solution of this body in dilute hydrochloric acid, needle-shaped crystals of phenylamidoacetamide hydrochloride are obtained. This substance has been previously described by Plöchl (*Ber.*, **13**, 2120). The free base has not been isolated, as the hydrochloride yields phenylamidoacetic acid, when acted on by acids or alkalis. *Barium and magnesium phenylamido-acetates*,  $\text{Ba}(\text{C}_6\text{H}_5\text{NO}_2)_2$ , and  $\text{Mg}(\text{C}_6\text{H}_5\text{NO}_2)_2 + \frac{1}{2}\text{H}_2\text{O}$ , crystallise in white plates, soluble in hot water. The *silver salt*,  $\text{AgC}_6\text{H}_5\text{NO}_2$ , forms slender prisms, insoluble in water. Phenylamidoacetic acid is converted into mandelic acid by the action of sodium nitrite on its hydrochloride. On dry distillation, phenylamidoacetic acid splits up into benzylamine and benzylammonium benzylcarbamate,  $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{COO}\cdot\text{CH}_2\text{Ph}\cdot\text{NH}_2$ . The latter compound crystallises in glistening plates (m. p.  $99^\circ$ ), soluble in alcohol and in water.

*Acetone cyanhydrin* was not obtained in the pure state. The crude product is converted into  $\alpha$ -amido-isobutyronitril by treatment with alcoholic ammonia at  $50$ — $60^\circ$ . By the action of strong hydrochloric acid at the ordinary temperature, and afterwards of dilute hydrochloric acid at a higher temperature, on this alcoholic solution, the hydrochloride of  $\alpha$ -amidoisobutyric acid is produced. As the acid is soluble in water, it is prepared by boiling its hydrochloride with silver oxide. This acid has the formula  $\text{COOH}\cdot\text{CMe}\cdot\text{NH}_2\text{Me}$ , and is identical with the amidodimethylacetic acid of Urech (*loc. cit.*) and Heintz (*Annalen*, **198**, 42). By the action of sodium nitrite on the hydrochloride,  $\alpha$ -hydroxyisobutyric acid (m. p.  $78^\circ$ ) is obtained.

On saponification, diethylketone cyanhydrin yields hydroxydiethylacetic acid,  $\text{COOH}\cdot\text{CEt}_2\cdot\text{OH}$  (m. p.  $80^\circ$ ), which is identical with the diethoxalic and diethylglycollic acids of Frankland and Duppa (*Annalen*, **135**, 25) and of Henry (*Ber.*, **5**, 950).

When the nitril obtained by the action of alcoholic ammonia on diethylketone cyanhydrin is treated with hydrochloric acid, it is converted into the hydrochloride of amidodiethylacetic acid,  $\text{COOH}\cdot\text{CEt}_2\cdot\text{NH}_2\cdot\text{HCl}$ , which crystallises in thick white prisms. The free acid forms glistening plates or prisms, soluble in water and alcohol, but insoluble in ether. When cautiously heated, it sublimes without melting; when suddenly heated, it decomposes into carbonic anhydride and an amine. The acid is isomeric with leucine, and bears a strong resemblance to  $\alpha$ -amido-isobutyric acid in its properties. The silver salt,  $\text{AgC}_6\text{H}_{12}\text{NO}_2$ , crystallises in white shining plates.

W. C. W.

**Amido-acids from Anisaldehyde and from Acetophenone.**

By F. TIEMANN (*Ber.*, **14**, 1976—1982).—If anisaldehyde cyanhydrin is left in contact with strong hydrochloric acid for 12 hours, the amide of paramethoxymandelic acid,  $\text{CH}_3\text{O.C}_6\text{H}_4.\text{CH}(\text{OH}).\text{CONH}_2$ , is deposited as a crystalline mass, together with a resinous body. After the latter is removed by digestion with ether and the residue is recrystallised from alcohol, the amide is obtained in small scales (m. p.  $159^\circ$ ).

*Paramethoxymandelic acid* is prepared by dissolving crude anisaldehyde cyanhydrin in sufficient alcohol to prevent the formation of a turbidity, when the solution is mixed with eight times its volume of hydrochloric acid (sp. gr. 1.10), diluted with an equal bulk of water. The mixture is boiled for six hours in a flask fitted with a reflux condenser, fresh quantities of hydrochloric acid being added from time to time. The alcohol in the liquid is removed by distillation and the residue is filtered, diluted with water, and evaporated to expel a portion of the hydrochloric acid, and extracted with ether. The oil which remains on evaporating the extract is dissolved in ether, and shaken up with dilute soda solution. The alkaline solution is acidified with hydrochloric acid, and again extracted with ether. This solution deposits the acid in ice-like crystals (m. p.  $93^\circ$ ), soluble in hot water, alcohol, ether, chloroform, and benzene. On exposure to the air, the acid is changed into a resinous mass. The copper and silver salts are amorphous; the barium salt is crystalline.

*Paramethoxyphenylamidoacetic acid*,  $\text{MeO.C}_6\text{H}_4.\text{CH}(\text{NH}_2).\text{COOH}$ , is formed when paramethoxyphenylamidoacetoneitril, prepared by the action of alcoholic ammonia on anisaldehyde cyanhydrin at  $70^\circ$  for 8 hours, is saponified by hydrochloric acid in the manner just described. The acid crystallises in needles, insoluble in alcohol and ether. It sublimes at  $225^\circ$  without melting. The hydrochloride crystallises in needles, and the copper salt is amorphous.

The formation of atrolactic acid from acetophenone cyanhydrin has been recently described by Spiegel (*Ber.*, **14**, 235, 1352). When acetophenone cyanhydrin is digested with the equivalent quantity of alcoholic ammonia at  $70^\circ$  in closed flasks for 8 hours, the nitril of  $\alpha$ -amidohydratropic acid is produced. On saponification with hydrochloric acid, the nitril is converted into the hydrochloride of the acid. The free acid,  $\text{HOOC.CMePh.NH}_2$ , forms needle-shaped crystals, insoluble in alcohol and ether, but soluble in water. The acid sublimes at  $260^\circ$  without melting. The salts are freely soluble in water; the copper salt forms pale blue needles. The hydrochloride also crystallises in needles. It is converted into atrolactic acid by the action of sodium nitrite solution.

W. C. W.

**Remarks on the three Preceding Papers.** By F. TIEMANN (*Ber.*, **14**, 1985).—The results contained in the three preceding papers show that amido-nitrils and amido-acids can easily be prepared from the cyanhydrins of aldehydes and ketones of the aromatic as well as the fatty series, without the formation of large quantities of bye-products.

The secondary amido-acids from the aldehydes are less soluble in water than the tertiary amido-acids prepared from the ketones.

W. C. W.

**Ethylic Benzylchloromalonate-Benzyltartronic and Phenyl-lactic Acids.** By M. CONRAD (*Annalen*, 209, 241—248).—The author points out that the method by which he accomplished the synthesis of benzyltartronic and phenyllactic acids from ethylic chloromalonate (Abstr., 1881, 168) may be advantageously used as a mode of preparing these acids. W. C. W.

**Synthesis of Organic Acids by the Electrolysis of Water by means of Carbon Electrodes.** By A. BARTOLI and G. PAPASOGLI (*Chem. Centr.*, 1881, 327—328).—During an investigation of the laws of galvanic polarisation, Bartoli observed that when graphite, gas-carbon, or charcoal is employed as the positive electrode, it in course of time undergoes considerable decomposition, falling as a fine powder to the bottom of the voltameter, whilst no such decomposition is observed when the carbon forms the negative electrode. The authors have investigated the cause of this phenomenon, and have found that the volume of gas given off from the positive carbon electrode is much less than when this electrode is of platinum. The oxygen which has thus disappeared must, therefore, have combined with the carbon of the electrode. Similar phenomena are observed in dilute sulphuric and acetic acids, and in solutions of potash or soda; whilst in the case of solutions of ammonia, or of the neutral or acid carbonates of sodium and potassium, the normal quantity of oxygen appeared at the positive electrode. The nature of the carbon forming the positive electrode also influences the results.

Among the products obtained when the electrolyte consisted of distilled water or of potash solution and the positive electrode of gas-carbon or of graphite, were mellitic and hydromellitic acids. In this connection, it is worthy of note that Schultze (*ibid.*, 1871, 643) also obtained mellitic acid by oxidising carbon with permanganic acid. T. C.

**Colouring Matter from Dimethylaniline and Chloranil.** By H. WICHELHAUS (*Ber.*, 14, 1952—1953).—The bluish-violet colouring matter which is produced when dimethylaniline is acted on by chloranil, tri- or tetra-chloroquinones, or by dichloronaphthoquinone, yields, on reduction with tin and hydrochloric acid, a colourless base,  $C_{16}H_{20}N_2$ , or  $C_{12}H_8Me_2N_2$ . This substance is deposited from alcohol in shining plates (m. p.  $173^\circ$ ), soluble in ether, benzene, chloroform, glacial acetic acid, and in hot alcohol. The hydrochloride forms colourless deliquescent crystals, which turn blue on exposure to the air. With platinum tetrachloride, it yields a double salt crystallising in needles,  $C_{16}H_{20}N_2 \cdot 2HCl \cdot PtCl_4$ .

The base unites with two molecules of methyl iodide, forming  $C_{16}H_{20}N_2 \cdot 2MeI$ . This compound is freely soluble in water, but less soluble in alcohol. It is decomposed by moist oxide of silver, yielding a powerful base, whose hydrochloride unites with platinum chloride, forming  $C_{16}H_{20}N_2(CH_3O)PtCl_6H_2$ . W. C. W.

**Gallein and Coerulein.** By K. BUCHKA (*Annalen*, 209, 249—277).—Gallein was first prepared by Baeyer (*Ber.*, 4, 455) by heat-

ing together phthalic acid and pyrogallol; on treating it with sulphuric acid coerulein is formed. The formula  $C_{20}H_{14}O_8$  was assigned to gallein. On heating to  $180^\circ$  it lost water, and was converted into its anhydride,  $C_{20}H_{12}O_7$ , or  $CO<\overset{C_6H_4}{\underset{O}{-}}>C[C_6H_2(OH)_2]_2:O$ . This for-

mula appears to be confirmed by the fact of a tetra-acetyl compound being formed when this body is heated with acetic anhydride. Its behaviour, however, with reducing agents is not explained by the above formula. In contact with potash and zinc-dust in the cold, it takes up two atoms of hydrogen; the product, if the above constitution were correct, should be analogous to phenolphthalin, possess acid properties, and be converted by means of strong sulphuric acid into a product analogous to phenolphthalidin. The reduced gallein, however, has no acid properties, and dissolves in cold sulphuric acid, being thrown down unchanged by addition of water. On the other hand, by further reduction, it takes up two more atoms of hydrogen, and is converted into a strongly acid body, which by the action of cold sulphuric acid is converted into coerulein, a compound analogous to phenolphthalidin. This product of a second reduction, called by the author *gallin*, must therefore stand in the same position as phenolphthalin, and the question of the constitution of the body intermediate between gallin and gallein, termed *hydrogallein*, naturally arose. The acetyl derivative of this compound is identical with that obtained from gallein, containing four acetyl-groups. We must therefore either assume that in the formation of gallein a direct combination occurs between the two phenyl-groups of the pyrogallol residue, which is broken up on the one hand by the addition of two atoms of hydrogen, and on the other by the action of acetic anhydride, an assumption for which there is no precedent, or that two of the hydroxyl-groups have been oxidised, giving rise to a quinone, as is known to be the case in the formation of cedraret. Gallein would then have the constitutional formula,  $CO<\overset{C_6H_4}{\underset{O}{-}}>C<\overset{C_6H_2(OH)}{\underset{C_6H_2(OH)}{-}}>O_2\}O$ , and hydrogallein,  $CO<\overset{C_6H_4}{\underset{O}{-}}>C[C_6H_2(OH)_2]_2:O$ , an assumption which explains entirely its formation and properties.

That a tetra-acetyl compound should be obtained from gallein appears to be against the presence of a quinone-group. On the examination of the behaviour of quinone and chloranil, it was however found to be quite possible to introduce the acetyl-group, and split up the quinone formation by means of acetic anhydride; the above constitution of gallein therefore presents no difficulty on this head.

By the further reduction of hydrogallein, gallin,



is produced, whilst on still further reduction, a body termed *gallol*, analogous to phthalol, and having the constitutional formula,



is formed. With acetic anhydride gallin gives a tetra-, and gallol a pent-acetyl compound. By fusion with an alkali, gallein is decom-

posed, like phenolphthaleïn, into benzoic acid and the anhydride of a pyrogallol ketone,  $\text{CO}[\text{C}_6\text{H}_2(\text{OH})_2]_2 : \text{O}$ .

By treating gallin with concentrated sulphuric acid, *coerulin* is formed in the same manner as phenolphthalidin is formed from phenolphthalin; its formula may be represented thus:  $-\text{C}_6\text{H}_4 < \begin{array}{c} \text{C} \\ \text{C}(\text{OH}) \end{array} \begin{array}{c} \text{C}_6\text{H}_2(\text{OH})_2 \\ \text{C}_6\text{H}(\text{OH})_2 \end{array} > \text{O}$ , it gives a tetracetyl derivative, phenolphthalidin giving a diacetyl compound: in both cases the hydroxyl attached to the middle carbon atom takes up no acetyl-group. By oxidation *coerulin* passes over into *coeruleïn*: this can be obtained direct from *galleïn* by heating with concentrated sulphuric acid. *Coeruleïn* therefore contains a quinone-group, and considering it analogous to phenolphthalideïn, should be formulated thus:  $-\text{C}_6\text{H}_4 < \begin{array}{c} \text{C}(\text{OH}) \\ \text{CO} \end{array} \begin{array}{c} \text{C}_6\text{H}_2(\text{OH}) \\ \text{C}_6\text{H}_2(\text{OH}) \end{array} > \text{O}_2 > \text{O}$ .

On treatment with acetic anhydride, however, it yields only a triacetyl compound. We must, therefore, either assume that the quinone-group has remained unaltered, and that the hydroxyl in the middle carbon-atom has been replaced by acetyl, an assumption for which there is no ground, or that in the formation of *coeruleïn* a loss of one molecule of water has taken place, the formula being really

represented thus:  $\text{C}_6\text{H}_4 < \begin{array}{c} \text{O} \\ | \\ \text{C} \\ \text{CO} \end{array} \begin{array}{c} \text{C}_6\text{H}_2 \\ \text{C}_6\text{H}(\text{OH}) \end{array} > \text{O}_2 > \text{O}$ . This assumption

receives support from the fact that triacetylcoeruleïn is formed by the oxidation of tetracetylcoeruleïn, which could not very well yield a triacetyl compound containing the quinone-group.

On heating *coeruleïn* with zinc-dust, phenylanthracene is obtained.

*Galleïn and its Derivatives based on Triphenylmethane.*—To prepare *galleïn*, phthalic anhydride is heated at  $190^\circ$  to  $200^\circ$  with pyrogallol; it may be purified by redissolving in alcohol and precipitation: it is then converted into the acetyl compound, which is purified by repeated crystallisation, decomposed with potash, and the pure *galleïn* precipitated by hydrochloric acid and dried. Prepared in this way, it forms a brown powder or small crystals, having a greenish-yellow metallic lustre. It is almost insoluble in water, easily in alcohol with dark red colour: ether, glacial acetic acid, and acetone scarcely dissolve it, and it is nearly insoluble in benzene and chloroform. It dissolves unchanged in cold sulphuric acid, but on heating is converted into *coeruleïn*. Its salts with alkalis are crystalline bodies of greenish metallic lustre, giving red or violet solutions which turn blue on addition of more alkali. The barium and calcium salts are soluble, the aluminium salt a red-violet precipitate.

*Tetracetyl-galleïn* is produced by heating *galleïn* and acetic anhydride together with sodium acetate in sealed tubes at  $150^\circ$ , and is thrown down by water as a brown oil, which readily solidifies into a crystalline mass. It is purified by recrystallisation from benzene; it is also soluble in chloroform, glacial acetic acid, alcohol and acetone, but insoluble in ether. Hot water, alkalis, and sulphuric acid decompose it: (m. p.  $247^\circ$  to  $248^\circ$ ).

*Tetrabenzoylgallein* is obtained by heating gallein with benzoic chloride. The brown oily product is washed, boiled with ether, the ethereal solution shaken up with soda, evaporated, and the yellow residue purified by crystallisation from acetone. The melting point of tetrabenzoylgallein is  $231^{\circ}$ ; it is easily decomposed by potash.

*Dibromogallein*.—Gallein suspended in glacial acetic acid is treated with bromine: after all is dissolved, the solution is evaporated, and dibromogallein is obtained in gold-green crystals. It is easily soluble in alcohol, glacial acetic acid, and acetone, but with difficulty in benzene and chloroform. In fixed alkalis it dissolves with blue and red, and in ammonia with violet colour. Heated with acetic anhydride it yields *tetracetyldibromogallein* in colourless crystals (m. p.  $234^{\circ}$ ).

*Hydrogallein* is formed when an alkaline solution of gallein is reduced in the cold with zinc-dust. The solution is acidified, and the hydrogallein shaken out with ether. It dissolves in alkalis with blue colour, and is easily oxidised to gallein, except when in acid solution. On treatment with acetic anhydride, the same acetyl compound is obtained as from gallein.

*Gallin* is best prepared by heating a solution of gallein in ammonia and gradually adding zinc-dust until a sample of the liquid acidified with sulphuric acid and shaken with ether, leaves on the evaporation of the ether a residue which is changed into coerulein in the cold by concentrated sulphuric acid, yielding a green solution with ammonia. Gallin expels carbonic anhydride from carbonates: it forms with acetic anhydride a tetracetyl compound, which has acid properties, and is easily soluble in alcohol (m. p.  $220^{\circ}$ ).

*Gallol* is obtained by heating an acid solution of gallein for some time with dilute sulphuric acid and zinc-dust. Heated with acetic anhydride, it yields a pentacetyl derivative (m. p.  $230^{\circ}$ ).

*Anhydropyrogallolketone*.—This body is formed along with benzoic acid, by fusing gallein with potash. It is a brown substance, soluble in alkalis, and yielding a tetracetyl compound in the ordinary way (m. p.  $237^{\circ}$ ).

*Derivatives of Gallein based on Phenylanthracene. Coerulein*.—On heating a solution of gallein in concentrated sulphuric acid at  $200^{\circ}$ , a dark olive-brown solution is formed, from which coerulein is thrown down by water as a black precipitate: it is purified by treatment with alcohol. It is scarcely soluble in water, alcohol, or ether, but more easily in glacial acetic acid and alkalis, forming in the latter case brilliant green solutions. Heated with acetic anhydride, it yields a triacetyl compound in red needles, which is also obtained by the oxidation of tetracetyl coerulein. Its acetic acid solution is decolorised by zinc-dust.

*Coerulein*.—Concentrated sulphuric acid converts gallin into coerulein: the latter may, however, be better prepared by reduction of an ammoniacal solution of coerulein with zinc-dust: the acidified solution is extracted with ether, on the evaporation of which coerulein is left behind as a red body, which oxidises in the air to coerulein. On account of its instability, its acetyl derivative cannot be prepared



directly, but is best obtained by heating triacetylcoerulein with acetic anhydride and zinc-dust; it crystallises from glacial acetic acid in fine yellow needles (m. p.  $256^{\circ}$ ) containing four acetyl-groups. Heated on a water-bath with glacial acetic acid and potassium dichromate, it is easily oxidised to triacetylcoerulein. Heated with zinc-dust in a stream of hydrogen, coerulein yields a yellow oil, which crystallises in yellow plates from alcohol, and shows the reactions of phenylanthracene, being converted by potassium dichromate and sulphuric acid into phenyloxanthranol.

J. K. C.

**Benzoyl and Benzyl Derivatives of Diphenyl.** By N. WOLF (*Ber.*, **14**, 2031—2032).—The residue which remains after the product of the action of aluminium chloride on a mixture of benzoic chloride and diphenyl, has been treated with water and sodium hydroxide, consists of a mixture of mono- and di-benzoyldiphenyl. The resinous mass is treated with a small quantity of alcohol, which dissolves out monobenzoyldiphenyl,  $C_{12}H_9.C_6H_5.CO$ , and other compounds. The residue is boiled with a large quantity of alcohol in a flask fitted with an upright condenser. The alcoholic solution on cooling deposits colourless crystals (m. p.  $218^{\circ}$ ) of dibenzoyldiphenyl,  $C_{12}H_8.Bz$ . This substance is soluble in ether and in hot benzene and hot alcohol. On reduction with hydriodic acid and amorphous phosphorus at  $170^{\circ}$ , dibenzoyldiphenyl,  $C_{12}H_8(CH_2.C_6H_5)_2$ , is obtained in glistening plates (m. p.  $113^{\circ}$ ) soluble in alcohol.

Monobenzoyldiphenyl (m. p.  $106^{\circ}$ ) is soluble in benzene, ether, and in hot alcohol.

W. C. W.

**Triphenylmethane.** By E. and O. FISCHER (*Ber.*, **14**, 1942—1944).—The method of preparing triphenylmethane, recently described by Schwarz (*Ber.*, **14**, 1516; this vol., 912), was discovered by Friedel and Crafts (*Compt. rend.*, 1877, 1450) four years ago. The hydrocarbon,  $C_{19}H_{14}$ , obtained by the dry distillation of triphenylmethane bromide, which is described by Schwarz as diphenylphenylene-methane, is identical with diphenylenephenylmethane (*Ber.*, **11**, 613 and 817). Triphenylmethane boils one or two degrees below the boiling point of mercury (*Ann. Chim. Phys.*, **14**, 409), and not at  $330^{\circ}$ , as stated by Schwarz.

*Triphenylcarbinol* is best prepared by gradually adding an excess of chromic anhydride to a warm solution of the hydrocarbon in five times its weight of glacial acetic acid. The reaction is complete when water throws down a crystalline precipitate from the solution, which does not melt on boiling.

W. C. W.

**Constitution of Naphthalene Derivatives.** By BEILSTEIN and KURBATOW (*Chem. Centr.*, 1881, 359—361).—The authors propose the following method for the determination of the constitution of naphthalene derivatives:—An  $\alpha$ -derivative of naphthalene,  $C_{10}H_7R$ , on oxidation will give an  $R\alpha$ -phthalic acid, and from the constitution of the latter, that of the original naphthalene derivative may be found. Thus bromonaphthalene on oxidation gives bromophthalic acid; and since phthalic acid on oxidation is easily converted into benzoic acid, it is

to be expected that bromophthalic acid would give ortho- and meta-bromobenzoic acids. The authors have solved the first part of this problem, viz., the oxidation of the naphthalene derivatives, but have not yet succeeded in converting the substituted phthalic acids into substituted benzoic acids.

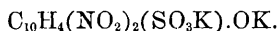
*Naphthalene* on oxidation with chromic acid in acetic acid solution gives not only naphthaquinone, as found by Groves, but also phthalic acid, and by using nitric acid, about 40 per cent. of the theoretical yield of the latter acid is obtained. *β-Naphthalenesulphonic acid* on oxidation with permanganate gives phthalic acid amongst other products. The calcium salt also gives phthalic acid on oxidation with chromic acid, whilst the free *β*-acid under these circumstances does not give phthalic acid but naphthaquinonesulphonic acid. *α-Naphthalenesulphonic acid* on oxidation with permanganate gives phthalic acid. *α-Bromonaphthalene* by oxidation with chromic acid gives phthalic acid amongst other products. *α-Nitronaphthalene* is but slowly attacked by permanganate, and still less by chromic mixture; by chromic acid in acetic acid solution, it gives nitrophthalic acid and an indifferent body,  $C_8H_5NO_7$  (nitrophthalic aldehyde?): the latter forms crystals (m. p.  $135^\circ$ ) which are but little soluble in hot water and still less in cold, but easily soluble in alcohol, acetic acid, benzene, carbon bisulphide, and chloroform. By oxidation, which only takes place with great difficulty, it gives nitrophthalic acid. The nitrophthalic acid forms hard crystals (m. p.  $212^\circ$ ), which are easily soluble in water, and on reduction it gives metamidobenzoic acid. This method is a very convenient one for obtaining nitrophthalic acid, as the product is not accompanied by any isomeric acid. The above facts prove that in nitronaphthalene the nitro-group occupies the same position as in ordinary nitrophthalic acid.

*α-Dinitronaphthalene*, on oxidation with dilute nitric acid at  $150^\circ$ , gives symmetrical dinitrobenzoic, picric, and ordinary nitrophthalic acids, but no dinitrophthalic acid. The two nitro-groups in *α*-dinitronaphthalene are therefore attached to two different benzene rings, and in one of these rings the nitro-group is in the same position as in *α*-nitronaphthalene.

*β-Dinitronaphthalene*, on oxidation with dilute nitric acid, gives dinitrophthalic acid (m. p.  $226^\circ$ ), together with a little nitrophthalic acid (possibly arising from a trace of admixed mononitronaphthalene), and on further oxidation 1 : 3 : 5 dinitrobenzoic acid and picric acid. From this it follows that in *β*-dinitronaphthalene both nitrogen-groups are attached to the same benzene ring; this shows that the assumption of Reverdin and Nölting to the contrary is incorrect.

T. C.

**Dinitronaphtholsulphonic Acids.** By P. LAUTERBACH (*Ber.*, 14, 2028—2031).—Naphthalene yellow of the “Badische Anilin und Soda Fabrik,” is potassium dinitronaphtholsulphonate,



By boiling this substance with strong hydrochloric acid, the dinitrosulphonic acid is obtained in long yellow needle-shaped crystals. The

sodium and ammonium salts are freely soluble, the barium and lead salts sparingly soluble in water.

*Nitroamidonaphtholsulphonic acid*,  $C_{10}H_4(NO_2)(NH_2)(OH).SO_3H$ , prepared by the reduction of naphthalene yellow with stannous chloride, crystallises in golden scales, sparingly soluble in hot water.

*Diamidonaphtholsulphonic acid*,  $C_{10}H_4(NH_2)_2(OH).SO_3H$ , is deposited in plates when naphthalene yellow is treated with tin and hydrochloric acid. On oxidation with ferric chloride, it yields *di-imidonaphtholsulphonic acid*,  $SO_3H.C_{10}H_4(NH_2)<\overset{NH}{\underset{-O-}{\text{>}}}$ , which crystallises in red

microscopic needles. It is precipitated from its solution in alkalis by the addition of an acid. A blood-red solution is formed when dinitronaphtholsulphonic acid is treated with ammonia and zinc-dust. It deposits white shining needles, which appear to have the composition  $C_{20}H_{18}N_3O_{12}S_2$ .  
W. C. W.

**Rosin-oil.** By A. RENARD (*Bull. Soc. Chim.* [2], **36**, 215—216).—The volatile oil obtained by distilling colophony yields the following fractions:—(1.) B. p.  $103-106^\circ$ , consisting of heptene,  $C_7H_{12}$ . (2.) B. p. about  $150^\circ$ , containing a terebenthene,  $C_{10}H_{16}$ , closely resembling ordinary terebenthene, and two hydrocarbons,  $C_{10}H_{16}$ , one of which is converted into a polymeride by the action of sulphuric acid, whilst the other is not attacked. (3.) B. p.  $169-173^\circ$ , containing two hydrocarbons,  $C_{10}H_{16}$ , one being polymerised by sulphuric acid, whilst the other is unacted on. This fraction did not contain cymene, the cymenesulphonate obtained by Kelbe, and also by the author having been formed by the action of sulphuric acid on terebenthene. The fraction boiling between  $106$  and  $150^\circ$ , is very small, but contains two hydrocarbons,  $C_8H_{14}$ , b. p. about  $130^\circ$ , and  $C_8H_{16}$ , b. p. about  $140^\circ$ , which appears to exist in two isomeric modifications, one polymerised by sulphuric acid, the other not attacked.

C. H. B.

**Oil of Erigeron Canadense.** By F. VIGIER and C. CLOEZ (*J. Pharm.* [5], **4**, 333—336; see Abstr., 1881, p. 1151).—Freshly prepared oil of erigeron is a clear yellow liquid with a characteristic herbaceous odour, and a persistent sharp bitter taste, similar to that of American essence of peppermint. Exposed to the air, it rapidly oxidises with formation of a brown deposit. When distilled, the greater part passes over between  $175$  and  $177^\circ$ , and a reddish-brown oxidation product is left in the retort. After distillation, it is a colourless very mobile liquid, leaves no stain on paper after evaporation, does not take fire on approach of a light, but burns with a smoky flame when thrown on glowing coals. It has the composition  $C_8H_8$ , and is an isomeride of essence of terebenthene. Sp. gr. at  $10 = 0.848$ ; molecular rotatory power  $[\alpha]_D = 6^\circ 15'$ ; refractive index,  $1.47335$ . When treated with a current of dry hydrochloric acid gas, it turns black, and after some time suddenly solidifies to a crystalline mass of the composition  $C_8H_8HCl$ . The formation of this body would indicate that oil of erigeron is an isomeride of lemon-oil, and has the formula  $C_8H_8$ . In this reaction no liquid camphor is formed. Oil of erigeron, when gently heated, is violently attacked by nitric acid,

with formation of a yellow viscous resin, which dissolves in potassium hydroxide solution, colouring it deep red. Sulphuric acid gives a black coloration, but iodine does not cause an explosion when brought in contact with the oil. Pure chloral hydrate is without action on the oil, but in presence of hydrochloric acid a green coloration is produced, which changes to greenish-brown on gently heating. Oil of erigeron is not saponified by potash, but is coloured orange-red: when it is heated, the colour darkens, and the oil is partly converted into a reddish-purple viscous mass. With the freshly distilled oil, this reaction is not well marked, but it readily takes place with the slightly oxidised substance. Essence of peppermint does not give this reaction, but forms, with the alkali, a white emulsion, which, when heated, acquires a clear pale-yellow colour. The reaction may therefore be employed to detect the presence of oil of erigeron in essence of peppermint. Oil of erigeron is completely insoluble in alcohol of 85° at 15°, whereas essence of peppermint readily dissolves. When a mixture of the two oils is agitated with an equal volume of alcohol of 85°, it becomes milky, and after 24 hours the insoluble oil separates out. In this way 8–10 per cent. of oil of erigeron may be detected in essence of peppermint. Essence of *Eucalyptus globulus* and essence of turpentine behave in the same way. Oil of erigeron is a valuable remedy in all forms of hæmorrhage, in diarrhœa, dysentery, and the intestinal hæmorrhage in typhoid fever. C. H. B.

**Constituents of "Maracaibo" Copaïba Balsam and of the Commercial so-called Copaïbic and Metacopaïbic Acids.** By R. BRIX (*Monatsh. f. Chem.*, 2, 537–517).—The results of previous investigations on copaïba balsam have differed, some with regard to the properties of its terpene, others with reference to the crystalline acids and amorphous resins to be obtained from it. The author's intention is to clear up these differences.

The copaïba balsam used in these experiments was a perfectly clear thick liquid of a brownish-yellow colour; its refractive index was 1·51. It was distilled with steam. The volatile oil, after drying over calcium chloride, was repeatedly boiled up with sodium, the colourless liquid being distilled off each time and re-treated until the metal remained unattacked; it was now of a very pale yellow colour, b. p. 250–260°, sp. gr. 0·892 at 17°, and refractive index = 1·503. Analysis led to the formula  $C_{26}H_{32}$ . This terpene absorbs water when boiled with it, forming a tough brown resinous mass, and on exposure to the air it becomes viscid without change of colour. It did not give a crystalline hydrochloride, but by dry hydrochloric acid it was turned at first rose-red, and when saturated, dark violet-blue, soon changing to green-brown in the air, at the same time giving off hydrochloric acid. With nitric acid, and a mixture of that acid with sulphuric acid, the results were the same as Strauss obtained, viz., a resinous mass. Oxidised with chromic mixture it gave acetic and terephthalic acids. The residues from the treatment of the volatile oils with sodium, described above, yielded on careful distillation a deep blue oil (b. p. 252–260°) of the formula  $3C_{26}H_{32}, H_2O$ , easily soluble in absolute alcohol, ether, and fatty oils. Its refractive index is 1·496. Exposed to light and

air it becomes discoloured and viscid. By warming with phosphoric anhydride, it is converted into the terpene.

The resins left behind by the distillation with steam contain two hard and one soft resin, all of which are amorphous and show slight acid properties, and in addition to these, very small quantities of a crystalline acid, probably identical with Strauss's metacopaibic acid.

In conclusion the author points out that the so-called copaibic and meta-copaibic acids which enter into commerce, are really obtained from gurgun balsam, and are identical. This body has the formula  $C_{20}H_{30}O_2$ , is soluble in ether and alcohol; it is precipitated by water from the alcoholic solution in beautiful long needles of a silky lustre (m. p.  $126-129^\circ$ ), and has no acid properties. It forms a diacetyl-derivative,  $C_{20}H_{28}O_2\cdot\bar{A}c_2$ , soluble in ether and alcohol, and crystallising in small colourless needles, which soften at  $60^\circ$  and melt at  $74-75^\circ$ .

D. A. L.

**Oxidation of Borneol Acetate.** By H. SCHRÖTTER (*Monatsh. Chem.*, 1881, 224-231).—Borneol acetate is dissolved in glacial acetic acid, treated with chromic anhydride, and the product, after washing, submitted to distillation. The fraction passing over between  $260^\circ$  and  $275^\circ$ , forms after purification white prismatic needles of the formula  $C_{12}H_{18}O_3$  (b. p.  $273.5$  corr.; m. p.  $69^\circ$ ), and has a vapour-density of 6.88. On boiling this substance with aqueous potash, an acetyl-group is removed and oxyisocamphor,  $C_{10}H_{16}O_2$ , obtained; it has a faint vanilla-like odour, sublimes readily, and melts with partial decomposition at  $248-249^\circ$ . On treating oxyisocamphor with phosphorous pentachloride, an oil of the formula  $C_{10}H_{14}Cl_2$  is obtained (most probably formed by elimination of HCl from a trichloride,  $C_{10}H_{15}Cl_3$ ). On oxidation with nitric acid, oxyisocamphor yields crystals of a substance whose properties agree with those of oxy-camphoric anhydride,  $C_{10}H_{14}O_4$ .

A. J. G.

**Borneolcarboxylic Acid and Camphocarboxylic Acid.** By J. KACHLER and F. V. SPITZER (*Chem. Centr.*, 1881, 359).—Baubigny obtained these compounds by the action of sodium and carbonic anhydride on camphor in solution, and assigned to the acid the formula  $C_{11}H_{16}O_3$ . The authors have obtained sodium-borneol,  $C_{10}H_{17}NaO$ , by the action of sodium on a solution of borneol, and by the action of carbonic anhydride have converted it into sodium borneolcarboxylate,  $C_{11}H_{17}NaO_3$ . Camphocarboxylic acid (m. p.  $123-124^\circ$ ) gives a sodium salt,  $C_{22}H_{31}NaO_6$ , and a barium salt,  $C_{22}H_{30}BaO_6$ , and is therefore a dibasic acid having the composition  $C_{22}H_{30}O_6$ . By the action of acetic chloride, it loses 2 mols. of water, and gives a crystalline compound,  $C_{22}H_{28}O_4$  (m. p.  $195-196^\circ$ ), which is insoluble in water; by the action of phosphoric anhydride dissolved in chloroform, it loses only 1 mol. of water, and forms a crystalline substance,  $C_{22}H_{30}O_5$  (m. p.  $265^\circ$ ), in which one atom of hydrogen may be replaced by a metal. Neither compound admits of reconversion into camphocarboxylic acid. By the action of phosphorus pentachloride, camphocarboxylic acid gives a crystalline chloride,  $C_{22}H_{28}Cl_2$  (m. p.  $45-45.5^\circ$ ).

Camphocarboxylic acid may also be obtained from dibromocamphor,  $C_{10}H_{14}Br_2O$ , by the action of sodium and carbonic anhydride.

T. C.

**The Catechins.** By C. ETTI (*Monatsh. Chem.*, **2**, 547—557).—The author has re-examined the catechins from Gambia and Pegu catechus (compare Gautier, this Journal, **34**, 515; and Liebermann and Tauchert, *Ber.*, **13**, 694), and finds that they are identical. He dried his substance over sulphuric acid, and, like Zwenger (*Annalen*, **37**, 320), who dried his at  $100^\circ$ , obtained numbers from analysis agreeing with  $C_{18}H_{18}O_8$ . Catechin loses water when dried at  $110$ — $115^\circ$ , or at  $100^\circ$  in a stream of hydrogen, the numbers from analysis now agreeing with Liebermann's (*loc. cit.*). It melts at  $140^\circ$  without further loss of water, and the fused substance dissolves in boiling water; the solution deposits crystals of catechin. At  $150$ — $160^\circ$  it loses more water, and is converted into an anhydride of the formula  $C_{36}H_{34}O_{15}$ , a brownish-red amorphous powder, insoluble in water, but soluble in alcohol, from which solution it is precipitated in crystals by lime-water. At  $170$ — $180^\circ$  this anhydride loses another molecule  $H_2O$ , forming another anhydride,  $C_{36}H_{32}O_{14}$ , which in its turn by further loss of water at  $190$ — $200^\circ$  becomes  $C_{36}H_{30}O_{13}$ . On treating a concentrated solution of catechin in dilute alcohol with diazobenzene chloride, a red crystalline precipitate is formed, which after recrystallisation and drying at  $90$ — $100^\circ$ , gave numbers for the formula  $(C_6H_5.N:N)_2C_{18}H_{16}O_8$ ; this azobody is stable in air, dissolves in alcohol, ether, and alkalis, and dyes silk brownish-yellow. Heated to  $140^\circ$  with dilute sulphuric acid in sealed tubes, the catechin yields the red catechin anhydride, catechol, and phloroglucinol; when fused with potash for a short time, these last two bodies are the only products, but on continuing the fusion dihydroxybenzoic acid (protocatechuic) is also formed (compare Gautier, this Journal, **33**, 64). The author finds that the numbers from a catechin described in a former communication, and to which he gave the formula  $C_{19}H_{18}O_8$ , agree equally well with the formula  $C_{19}H_{20}O_8$ , and as its properties are very similar to those of catechin, he thinks it probable that it is methylcatechin.

D. A. L.

**Chlorophyll.** By R. SACHSSE (*Chem. Centr.*, 1881, 169—175, 185—191, 236—240).—The amount of chlorophyll in plants is generally much under-estimated. From 125 kilos. of fresh leaves the author has obtained no less than 100 grams of phyllocyanin, which he considers to be the principal constituent of chlorophyll. The numerous attempts which have been made to explain the reduction of carbonic anhydride by the green colouring matter of leaves, have so far been without result, and the following hypothesis is therefore proposed:—Chlorophyll is not the cause of the reduction of carbonic anhydride under simultaneous action of light and protoplasm, as is generally supposed, but is itself the first product of that reduction, the chlorophyll so formed being at once converted into starch and other carbohydrates, which have been usually considered to be the first products of the reduction, and its place supplied by more chlorophyll, resulting from a further reduction of carbonic anhydride. This hypothesis the author endeavours to submit to the test of experi-

ment by trying whether pure chlorophyll can be made to yield carbohydrates by the action of reducing agents, and more especially sodium. For this purpose a quantity of fresh leaves was treated with alcohol and benzene, according to a method for which the original paper must be consulted, by which means the alcohol takes up chiefly the yellow colouring matters which accompany the chlorophyll, whilst the latter is dissolved by the benzene.

A solution of chlorophyll in benzene was treated with sodium, when, after a lapse of 8—14 days, a cloudiness appeared, and gradually assumed the form of a voluminous green precipitate, whilst the supernatant liquid was no longer green but golden-yellow, owing to the presence of a yellow colouring matter (A), which will be subsequently referred to. The green precipitate was a dark green, almost black, mass, of soapy consistence, and was readily soluble in absolute alcohol, forming a brilliant green beautifully fluorescent liquid; it also dissolved in water, forming a similar solution, but less fluorescent. On adding the solution of a metallic salt, *e.g.*, copper sulphate, to the aqueous solution, a dark green voluminous precipitate of the copper salt is obtained, whilst there remains in the filtrate a colourless amorphous body, which has almost the composition of a carbohydrate, but containing rather more hydrogen, and is partially converted by the action of acids into a substance showing the most important reactions of a sugar of the dextrose group. On slightly acidifying the aqueous solution of the original green or fluorescent colouring matter with hydrochloric acid, or on passing in a current of carbonic anhydride, the liquid assumes a golden-green cloudy appearance, which in the case of the hydrochloric acid, soon settles out as a distinct precipitate, whilst the colourless amorphous substance above referred to remains in solution. The principal constituent of the precipitate is an almost black colouring matter, to which the name phyllocyanin is given. Among the decomposition-products of the original green colouring matter by means of acids, are two substances which belong to a class of yellow colouring matters to be subsequently referred to, and another which is of a fatty nature.

The author thinks that the original green fluorescing body is homogeneous, but of a very complicated composition. On analysis, it gave, as the extremes of several determinations:—60·96—61·88 per cent. C, 9·21—9·39 H, 1·99 N, 10·46—11·00 ash (which contained sodium, phosphoric acid, and magnesium, but no iron).

Phyllocyanin, which really includes several different bodies of a very similar nature, is a dark green, almost black mass, which is insoluble in water, only sparingly soluble in benzene, and, however prepared, is always nitrogenous. It may be separated into three different substances by treatment with hot alcohol. These gave the following composition on analysis:—

	C.	H.	N.
A. Insoluble in alcohol	67·66—67·77	8·03—8·41	5·46—5·92
B. Difficultly soluble in alcohol . . . . .	69·32—69·71	6·75—7·30	8·24—8·56
C. Easily soluble in alcohol . . . . .	69·14—69·70	7·45—7·60	7·08—7·30

On oxidation with potassium permanganate in alkaline solution, phyllocyanin gives ammonia, oxalic, palmitic, and probably lactic, acetic, and three other acids, which appear to be nearly related to or identical with itaconic, citraconic, and mesaconic acids.

On dry distillation under diminished pressure, phyllocyanin gives palmitic aldehyde; whilst on dry distillation with lime, it gives palmitone,  $C_{31}H_{62}O$ , or possibly stearin; on treatment with bromine in aqueous solution, it is decomposed into ammonia, and at least three other bodies, one of which is easily soluble in benzene; the second insoluble in benzene, but easily soluble in alcohol; and the third insoluble in either solvent.

In the solid state the yellow colouring matter A, referred to above, forms a mass varying in colour from brown to yellow, or reddish-yellow, of a fatty nature, always free from nitrogen, and varying in composition between 65·88—70·90 per cent. C, 7·91—9·80 H, and 26·21—19·30 per cent. O. Two other colouring matters of a pale yellow were also obtained, although it is very doubtful whether these latter were derived from the chlorophyll, or only admixed impurity; one of them had a composition represented by the formula  $C_{26}H_{52}O_2$ . The author considers the yellow colouring matter as the connecting link between the green colouring matters and the true fats, and is also of opinion that several modifications of chlorophyll exist, and that each chlorophyll contains a phyllocyanin, a yellow colouring matter, and a body nearly related to the carbohydrates. T. C.

**Diquinoline.** By H. WEIDEL (*Monatsh. f. Chem.*, **2**, 491—506).—This paper describes an application of Anderson's reaction (*Annalen*, **154**, 270) to the preparation of diquinoline by the action of sodium on quinoline (compare C. G. Williams, this Journal, 1881, 613).

When 100 grams of quinoline are heated with 15 of sodium at  $192^\circ$  for two or three hours, the liquid changes in colour from yellowish-brown to dark violet-brown, and at the same time becomes viscid, and finally sets to a hard resinous mass. This product is dissolved in benzene; the solution poured off from the unattacked sodium and shaken up with water as long as the latter is coloured brown; the benzene is driven off on a water-bath; and the residue distilled. The fraction passing over above  $360^\circ$  solidifies to a crystalline mass impregnated with an oily substance; the oil is removed from the crystals by suction and washing with alcohol. The crystals are dissolved in moderately strong hydrochloric acid, and the hydrochloride recrystallised several times from dilute hydrochloric acid; ammonia sets free the base, which can be obtained pure by crystallising from alcohol. The author calls this  $\alpha$ -diquinoline,  $C_{18}H_{12}N_2$ ; it crystallises in colourless monosymmetrical leaflets,\* having a mother-of-pearl like lustre, moderately soluble in warm ether, benzene, chloroform, &c., easily in hot, scarcely in cold alcohol, insoluble in water; they melt at  $175\cdot5^\circ$  (uncorr.) and sublime (the sublimed substance melts at  $176$ — $177^\circ$ ). The boiling point is above  $400^\circ$ , when slight decomposition sets in. The alcoholic solution reacts neutral, and has a biting taste.

\* Measured by Brezina.



The *sulphate*,  $C_{18}H_{12}N_2 \cdot H_2SO_4 + H_2O$ , is a dull white crystalline powder, which turns yellow by exposure to light. This change of colour is greatly accelerated by heating to  $100^\circ$ ; it loses its 1 mol.  $H_2O$  at  $150^\circ$  when heated in the air, at  $120^\circ$  in a stream of hydrogen. It has a biting, pepper-like taste, and is decomposed by water.

The *hydrochloride*,  $C_{18}H_{12}N_2 \cdot 2HCl + 4H_2O$ , crystallises in long, slender, almost colourless, asbestos-like needles, losing the  $4H_2O$  and 1 mol.  $HCl$  at  $100^\circ$ , forming the salt  $C_{18}H_{12}N_2 \cdot HCl$ . It is also decomposed by water.

The *platinochloride*,  $C_{18}H_{12}N_2 \cdot 2HCl \cdot PtCl_4 + H_2O$ , forms light reddish-yellow microscopic needles, almost insoluble in water and hydrochloric acid; the  $H_2O$  goes off at  $105^\circ$ .

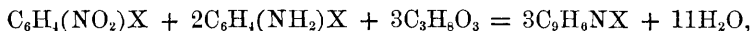
The *aurochloride*,  $C_{18}H_{12}N_2 \cdot HCl \cdot AuCl_3 + 2H_2O$ , light yellow needles, more soluble than the platinochloride; the  $2H_2O$  are given off at  $105^\circ$ . Methyl iodide combines slowly with  $\alpha$ -diquinoline at the ordinary temperatures, and quickly when heated at  $100^\circ$ , forming a *methiodide*,  $C_{18}H_{12}N_2 \cdot MeI$ , which crystallises in very brilliant, small, apparently rhombic needles, only slightly soluble in the ordinary solvents; heated to  $200^\circ$ , it turns brown, and melts at  $280$ – $286^\circ$ , with decomposition. Oxidation experiments on  $\alpha$ -diquinoline gave negative results. Quinoline from cinchonic acid also yields  $\alpha$ -diquinoline when treated with sodium. The author shows that the other product of the distillation of the cinchonic acid with lime (compare Koenigs, this Journal, **36**, 471–472), is also a diquinoline, and proposes to call it  $\beta$ -diquinoline. After purification by repeated crystallisation of its hydrochloride and decomposition of the same with ammonia, it crystallised from alcohol in small, perfectly colourless, broad, monoclinic needles (measured by v. Lang), melting at  $192.5^\circ$  (uncorr.). He thinks it highly probable that this body is identical with Japp and Graham's diquinolyline (this Journal, **39**, 174–176), from the action of benzoic chloride on quinoline. The yield of this body is very small; the largest quantity is produced when the distillation is conducted very quickly, and at as high a temperature as possible.  $\alpha$ -Diquinoline yields a disulphonic acid when heated in a sealed tube with fuming sulphuric acid at  $170^\circ$  for three or four hours; on pouring the contents of the tube into water, the acid separates out in microscopic needles.

The *potassium salt*,  $C_{18}H_{10}(KSO_3)_2 \cdot N_2 + 5H_2O$ , crystallised from 50 per cent. alcohol, forms small colourless needles, soluble in water, scarcely in absolute alcohol. It, as well as the acid, has a very bitter taste. The water of crystallisation goes off at  $150^\circ$ . Fused with potash, or digested with alcoholic potash, until a test, when acidified, gives off plenty of sulphurous anhydride, it forms a hydrate of the formula  $C_{18}H_{10}(OH)_2 \cdot N_2^*$ , which crystallises very badly, is deliquescent, decomposes in the air, and cannot be distilled without decomposition. In the preparation of the  $\alpha$ -diquinoline by the action of sodium on quinoline, the yield is about 34–38 per cent.; there is about 20–30 per cent. unattacked quinoline, and some other products which could be neither crystallised nor isolated.

D. A. L.

\* In the paper the formula given is  $C_{18}H_{10}(OH)_2$ ; evidently a misprint.

**Synthesis of the Quinoline Series.** By A. SCHLOSSER and Z. H. SKRAUP (*Monatsh. Chem.*, **2**, 518—538).—This is a continuation of the synthetical researches suggested by the equation—



in which X equals hydrogen or a monad radical; and by means of which one of the authors has already synthesised quinoline, toluquinoline, &c. (compare Abstr., 1881, 288 and 920). In this paper  $\text{X} = \text{COOH}$ ; the acids employed are the nitro- and amido-benzoic acids, and the products of the reaction are quinolinecarboxylic acids.

*Metaquinolinecarboxylic acid*,  $\text{C}_{10}\text{H}_7\text{NO}_2$ .—18 parts [1 : 3] nitrobenzoic acid, 30 parts [1 : 3] amidobenzoic acid, 50 parts glycerol, and 40 parts sulphuric acid are heated in a flask connected with a reflux condenser on a sand-bath for about six hours. The contents of the flask are now neutralised with barium hydrate, filtered, the filtrate precipitated with silver nitrate, and the precipitated silver salt suspended in dilute hydrochloric acid is decomposed with sulphuretted hydrogen. The hydrochloride obtained in this way is repeatedly recrystallised, and finally decomposed by water, setting free the acid, which when sublimed is a very white light powder of microscopic crystals, insoluble in ether, benzene, and carbon bisulphide, only partially soluble in water, sparingly in alcohol, and easily in dilute acids or alkalis. When very carefully heated, it sublimes without fusing in white woolly masses; its vapour has a sharp odour. Heated quickly, or with lime, it emits an odour of quinoline. It melts above  $360^\circ$ , and turns somewhat brown at this temperature. The neutral ammoniacal solution of metaquinolinecarboxylic acid gives the following salts:—With silver nitrate the *silver salt*,  $\text{C}_{10}\text{H}_6\text{NO}_2\text{Ag} + 2\text{H}_2\text{O}$ , a fine white powder, sparingly soluble in water, and only slightly sensitive to light; the  $2\text{H}_2\text{O}$  go off over sulphuric acid. With copper acetate the *copper salt*, which, when first precipitated, is light green and amorphous; it, however, gradually changes to a violet-blue salt, of the formula  $\text{C}_{10}\text{H}_6\text{NO}_2\cdot\text{CuOH} + 2\text{H}_2\text{O}$ , consisting of microscopic leaflets, losing their water at  $200^\circ$ . The *calcium salt*, precipitated by calcium chloride, has the formula  $[(\text{C}_{10}\text{H}_6\text{NO}_2)_2\text{Ca}]_2\cdot\text{C}_{10}\text{H}_7\text{NO}_2 + 6\text{H}_2\text{O}$ ; it forms long white needles, which are dry at  $200^\circ$ , and are easily soluble in water; another salt,  $(\text{C}_{10}\text{H}_6\text{NO}_2)_2\text{Ca} + 2\text{H}_2\text{O}$ , is produced when the free acid is treated with a small excess of lime and precipitated with carbonic anhydride. With lead acetate a white flocculent precipitate, which becomes crystalline on boiling; it is soluble in dilute acetic acid, and is deposited from the solution in nodules; with cobalt nitrate, on standing, large rose-red prisms; with nickel nitrate, a light green, flocculent salt, which becomes crystalline; with ferric chloride, and ferrous sulphate, yellow flocculent and amorphous greenish precipitates are produced. The *hydrochloride*,  $\text{C}_{10}\text{H}_9\text{NO}_2\cdot\text{HCl} + 1\frac{1}{2}\text{H}_2\text{O}$ , forms long colourless needles aggregated in stellate clusters, soluble in absolute alcohol and dilute hydrochloric acid, only very slightly in strong hydrochloric acid; water decomposes it. The  $1\frac{1}{2}\text{H}_2\text{O}$  goes off over sulphuric acid at higher temperatures, the hydrochloric acid is completely driven off without the substance melting. It is tolerably stable in air. The *platinochloride*,  $(\text{C}_{10}\text{H}_7\text{NO}_2\cdot\text{HCl})_2\cdot\text{PtCl}_4$ , crystallises in yellow micro-

scopic leaflets, which, when once formed, are very sparingly soluble in water and dilute hydrochloric acid.

*Paraquinolinecarboxylic acid* is prepared in a similar manner from the [1 : 4] nitro- and amido-benzoic acids. Crystals of the sulphate of this acid are deposited after cooling the product of the reaction. The free acid is a white powder composed of microscopic four-sided tablets; it is only very slightly soluble in water, but more so than the meta-acid, more soluble in alcohol, and easily in dilute acids and alkalis. It sublimes before melting, and distils without decomposing; it begins to soften at 260°, softens at 280°, turns brown, and then melts at 291—292°. The ammonium salt reacts with solutions of metallic salts as follows:—silver nitrate, a white precipitate; cobalt nitrate, reddish; and nickel nitrate, greenish flocculent precipitates. Potassium chromate, yellow granular crystals. Copper acetate, greenish-blue and slightly crystalline; ferric chloride, liver-brown, flocculent; ferrous sulphate, greenish, flocculent; barium chloride and calcium chloride, white crystalline salts. The *silver salt*,  $C_{10}H_6NO_2Ag$ , resembles the corresponding salt of the meta-acid. The *copper salt*,  $(C_{10}H_6NO_2)_2Cu + 2H_2O$ , is precipitated from the hydrochloride by copper acetate, and forms blue-green microscopic crystals, which lose their 2 mols.  $H_2O$  at 180°. The *calcium salt*,  $(C_{10}H_6NO_2)_2Ca + 2H_2O$ , prepared by boiling the free acid with precipitated calcium carbonate, forms slender prisms, slightly soluble in cold, easier in hot water. The water goes off at 270°. The *hydrochloride*,  $C_{10}H_7NO_2.HCl + H_2O$ , forms long transparent soft needles which, on standing in the mother-liquor for some time, change to a white crystalline powder. The  $H_2O$  and hydrochloric acid are given off over sulphuric acid, the former first. The *platinochloride* forms slender needles which soon change to large reddish-yellow plates, containing no water of crystallisation.

*Orthoquinolinecarboxylic acid* is prepared by heating together for three hours 9 grams [1 : 2] nitrobenzoic, 15 grams [1 : 2] amidobenzoic acid, 20 grams glycerol, and 25 grams sulphuric acid. The product is diluted with water, exactly precipitated with barium chloride, and the filtrate from the barium sulphate is evaporated down. The hydrochloride is purified by recrystallisation. The free acid crystallises in soft white needles soluble in hot water and alcohol, alkalis, and acids; melts at 186—187.5°, and, on further warming, can be sublimed without decomposition. The ammonium salt gives with silver and lead salts white crystalline precipitates; cobalt salts, flesh-red fine needles; nickel, apple-green scales; ferric chloride, brownish flocks, which soon change to a yellow powder; potassium dichromate, yellow needles; ferrous sulphate at first colours the solution dark purple-red, and then precipitates a purple-red to purple-brown powder, at the same time decolorising the solution. The *hydrochloride*,  $C_{10}H_7NO_2.HCl$ , forms glistening prisms of a slightly yellow colour, soluble in water. By evaporating down its aqueous solution, a basic salt,  $(C_{10}H_7NO_2)_2HCl$ , is formed, crystallising in large glistening, slightly red triclinic prisms (measured by v. Lang). The *platinochloride* is precipitated in small needles of an orange-yellow colour, soluble in hot water, less so in cold, and not at all in dilute hydrochloric acid. The *silver salt* has no water of crystallisation, and is

sparingly soluble in water. The *copper salt*,  $(C_{10}H_6NO_2)_2Cu + 3\frac{1}{2}H_2O$ , is a bluish amorphous precipitate which, on boiling, changes to light sky-blue needles, insoluble in water. The  $3\frac{1}{2}H_2O$  are lost at  $240^\circ$ . *Calcium salt*,  $[(C_{10}H_6NO_2)_2Ca]_2 + C_{10}H_6NO_2$ , crystallises in small needles, soluble in water.

An experiment was tried in which the amido-acid in the first experiment was replaced by aniline; the product was in this case principally quinoline.

In order to distinguish these acids which have the  $COOH$ -group in the benzene ring from those which have it in the pyridine ring, the author suggests the name "quinolinebenzcarboxylic acids."

D. A. L.

**Oxidation-products of Morphine.** By P. CHASTAING (*J. Pharm.* [5], 4, 338—343).—When an alcoholic solution of morphine is saturated with hydrochloric acid gas, and left at rest for 24 hours, morphine hydrochloride is obtained; but if, after saturation, the liquid is allowed to remain at rest several days, again saturated with the acid, and left for a further period of 15 days, ethylmorphine hydrochloride is formed. In order that this compound may be produced, it is necessary that the quantity of morphine present should be small compared with that of the alcohol and hydrochloric acid. If monohydrated sulphuric acid is added in considerable quantity to the alcoholic solution, the mixture after saturation with hydrochloric acid, left to itself for two days, and then slowly evaporated below  $85^\circ$ , the addition of ammonia produces a white precipitate which, when washed with water and dissolved in alcohol, rapidly turns green. On evaporation of the alcoholic solution by exposure to air, an amorphous substance is obtained, which gives all the general reactions of the alkaloids; is neutral to litmus, and has a taste less bitter than that of morphine; dissolves in acids and alkalis, but does not form crystallisable salts. It is oxymorphine hydrate,  $C_{17}H_{18}NO_4 + H_2O$ , and dissolves easily in water and alcohol, but is insoluble in chloroform and ether. When dissolved in alcohol and exposed to the air, it is gradually oxidised. This substance differs in its properties from the oxymorphine hydrate prepared by Schützenberger's process. It is a derivative of sulphomorphine.

The author, like Anderson, was unable to obtain a nitro-substitution derivative of morphine by the action of nitric acid. By slowly evaporating morphine twice with nitric acid of sp. gr. 1.42, and then heating the product on the water-bath until all nitrogen oxides were driven off, he obtained an acid of the composition  $C_{11}H_{11}NO_9$ ; by evaporating with nitric acid three times, the acid,  $C_{10}H_9NO_9$ , was obtained. This compound is not acted on by nitric acid of sp. gr. 1.42 at  $100^\circ$ . When it is heated with potash, methylamine is evolved, and if the solution of the alkalis is concentrated, almost the whole of the nitrogen is given off in this form. The potassium salt does not crystallise well, but appears to contain 4 atoms of the metal. The barium salt has the composition  $C_{10}H_5Ba_2NO_9 + 4H_2O$ , and is obtained as a white precipitate by adding baryta-water to an aqueous solution of the acid. The lead salt has a similar composition.

C. H. B.

**Double Salt of Quinine Hydrochloride and Urea.** By A. DRYGIN (*Chem. Centr.*, 1881, 245).—A solution of quinine hydrochloride dissolved in an equivalent quantity of hydrochloric acid, is treated with an equivalent quantity of urea. The solution solidifies very rapidly, and is heated to  $50^{\circ}$  until it is redissolved. On cooling, the crystalline mass is broken up into small pieces, allowed to drain on filters, washed with a small quantity of cold water, and dried in the air. The double salt consists of crystalline masses of needle-shaped rhombic prisms, grown together; it dissolves in equal parts of water at  $17-18^{\circ}$ . Analysis gave the formula  $C_{20}H_{24}N_2O_2 \cdot HCl + CH_4N_2O \cdot HCl + 5H_2O$ .

Quinidine and cinchonidine form double salts with urea; the former alone crystallises readily, the latter being very deliquescent. This latter property may be utilised as a mode of separating quinine from cinchonidine.

D. B.

**Hydroquinidine (Hydroconquinine).** By C. FORST and C. BÖHRINGER (*Ber.*, 14, 1954—1956).—A new alkaloïd,  $C_{20}H_{26}N_2O_2 + 2\frac{1}{2}H_2O$ , to which the name *hydroquinidine* is given, is formed by the action of potassium permanganate on quinidine. On evaporating the alcoholic solution of the crude product, a crystalline crust and a syrupy mother-liquor are left. The crystals are washed with ether-alcohol and recrystallised from alcohol. The base forms thin prismatic crystals, which rapidly effloresce on exposure to the air. It is sparingly soluble in ether. The alcoholic solution has an alkaline reaction, and is dextrogyratory. With chlorine-water and ammonia, the alcoholic solution produces a green coloration. A solution of the base in an excess of dilute sulphuric acid exhibits a blue fluorescence. The following salts were prepared: the *hydrochloride* and *neutral tartrate* crystallise in short needles, freely soluble in cold water; the *acid tartrate* is sparingly soluble in water. The *platinochloride*,  $C_{20}H_{26}N_2O_2 \cdot (HCl)_2 \cdot PtCl_4 + 2H_2O$ , forms orange-coloured needles;  $C_{20}H_{26}N_2O_2 \cdot HI$ , broad white needles, sparingly soluble in cold water. The *sulphate*,  $2(C_{20}H_{26}N_2O_2) \cdot SO_4H_2 + 12H_2O$ , forms efflorescent crystals.

W. C. W.

**Strychnine Hydrate.** By E. JAHNS (*Chem. Centr.*, 1881, 367—368).—Schützenberger has stated (*Chem. Centr.*, 58, 677 and 684) that ordinary strychnine is a mixture of three alkaloids, which differ from one another in amount of carbon, in their solubility in water, and in crystalline form; and was led to this conclusion from having observed, that on adding ammonia to a dilute solution of strychnine hydrochloride, first needles and subsequently octahedrons are precipitated. The author is unable to confirm this view, for he finds that the former crystals pass spontaneously into the latter, the transformation being easily seen under a microscope.

T. C.

**Preparation and Derivatives of Colchicine.** By J. HERTEL (*Chem. Centr.*, 1881, 501).—On heating colchicine,  $C_{17}H_{23}NO_6$ , with a mineral acid, it loses a molecule of water, and is converted into *colchicine*, and the latter by warming with water is reconverted into

colchicine. In the air it loses ammonia and water, being first converted into *colchicoresin*,  $C_{51}H_{60}N_2O_{15}$ , and finally into *betacolchicoresin*,  $C_{34}H_{39}NO_{10}$ . These latter products are found in the seeds of *Vinum colchici* which have been kept for some time, and are not inferior in their physiological action to colchicine.

J. K. C.

**Formula of Pilocarpine.** By P. CHASTAING (*J. Pharm.* [5], 4, 336—338).—Analyses of the platinochloride and of the carefully purified nitrate prove that the true formula of pilocarpine is  $C_{22}H_{16}N_2O_4$ , as stated by Harnach and Meyer. Pilocarpine nitrate may be perfectly freed from jaborine by treatment with absolute alcohol.

C. H. B.

**Preparation of Cocaïne.** By V. TRUPHÉME (*Chem. Centr.*, 1881, 447).—Cut coca leaves are digested with ether in Payen's extraction apparatus, the blackish-green solution is distilled off and evaporated, and the residue, which has a melting point of  $75^\circ$ , is dissolved in boiling water, with agitation. After filtration, the solution is treated with magnesia and evaporated. The residue is then mixed with amyl alcohol, from which cocaïne crystallises in pale yellow crystals, becoming colourless when recrystallised.

D. B.

**Constitution of Albuminoids.** By A. DANILEWSKY (*Chem. Centr.*, 1881, 503—504).—By the action of alkalis on pancreatin on albumin, several intermediate bodies are formed, the final product always being peptone.  $\beta$ -albumin is first produced, a body insoluble in water and warm alcohol, of weak acid reaction, and containing sulphur extractible by alkaline hydroxides, together with calcium and phosphorus. The bodies next formed belong to the protalbin group, and are more soluble in water and warm alcohol, more strongly acid, and free from calcium and phosphorus; their solutions give coloured residues when evaporated to dryness, and some of them lose their sulphur when heated with soda solution. Finally, we have the peptones, which combine with bases and acids, and yield no sulphides with alkalis. By the action of acids on pepsin,  $\beta$ -albumin is first formed, and then *syntonid*, a member of the albumin group, which neutralises acids, yields sulphide to alkaline hydroxides, and is insoluble in water; next in order comes the syntoprotalbin group, the members of which coagulate in the cold with acids; and finally the peptones. Tropaeolin was used as indicator in testing the reactions of the various bodies as they were formed, and hydrochloric acid and platinic chloride, which formed compounds rich in chlorine and platinum with basic bodies, and rich in platinum only with acid products. Both series of compounds can be formed from all kinds of albumin. So-called acid albumins are analogues of syntonid, and albuminates consist of various mixtures of natural albumins and protalbin bodies, which have been built up by the action of alkalis or ferments, and have the same characters as milk casein.

J. K. C.

**Albuminoids of Blood Serum.** By L. FRÉDÉRIQUE (*Chem. Centr.*, 1881, 484—485).—In the preparation of paraglobulin by pre-

cipitation of dilute serum with acetic acid, small quantities of a body called fibrinogen may be seen sticking to the walls of the vessel in flakes, which are not completely soluble in salt solution. When the paraglobulin is precipitated with magnesium sulphate, then redissolved and reprecipitated several times, an admixture of fibrinogen is not observed. Paraglobulin so prepared is a very stable body; its 2 per cent. aqueous solution has a specific lævorotatory power of  $47.8^\circ$ . The filtrate from paraglobulin was gently heated, and the remaining albuminoids precipitated by fractional coagulation; the greater part separated at  $40-50^\circ$ , and the rest at  $60^\circ$ . The former is perfectly soluble in water, has a lævorotatory power of  $57.3^\circ$ , and is termed by the author serin. By the aid of the known rotatory powers of paraglobulin and serin, the author calculates the percentage amounts of these in blood-serum. This method agrees very well with the results of quantitative estimation.

J. K. C.

**Yolk Pigments.** By R. MALY (*Chem. Centr.*, 1881, 485).—So-called lutein, the colouring matter of yolk of hen's eggs, was found to be present in large quantities in the eggs of shrimps, side by side with a relatively small amount of fat. Further investigation showed that lutein is a mixture of two colours, called vitellolutein and vitellorubin; the former yellow, and the latter red. They may be separated by heating the yolk extract with a little acid to boiling, and treating the precipitated albumin with petroleum, which dissolves out the yellow, and then with carbon bisulphide, which removes the red pigment; or by treating the alcoholic extract with baryta-water, which throws down the vitellorubin, and leaves the other in solution. Neither pigment contains nitrogen; the magnesium compound of vitellorubin is soluble with dark-red colour in ether, chloroform, and carbon bisulphide, and is precipitated by the addition of alcohol in red flakes. Vitellorubin gives a broad but weak absorption-band, containing the F line, whilst vitellolutein gives two narrow bands clearly distinct from each other.

J. K. C.

**Urochloralic Acid.** By E. KÜLZ (*Chem. Centr.*, 1881, 486—487).—This acid is found in the urine of any animal which has been dosed with chloroform. The sodium salt,  $C_8H_{12}Cl_3NaO_7$ , crystallises best; its solution has a reducing action, which is increased by boiling with hydrochloric or sulphuric acid. When a 5 per cent. solution of the salt is boiled with 5 per cent. hydrochloric acid for some hours in connection with a reflux condenser, the urochloralic acid is decomposed into a chlorinated body soluble in ether, and a dextrorotatory strongly reducing acid, probably a derivative of grape-sugar. Pure sodium urochloralate has no stupefying action when taken internally, and reappears for the most part in the urine unchanged. Trichloroacetic acid cannot be used as a source of urochloralic acid; hence Liebreich's theory of the action of chloral is probably false. From the urine of dogs which have been dosed with butyl-chloral, the author has succeeded in separating the potassium salt of urobetylchloralic acid in very fine crystals. The aqueous solution of this salt has a lævorotatory action, but does not reduce Fehling's solution until after

boiling with acid. Like urochloralic acid, it splits up on heating for some time with dilute hydrochloric acid, into a chlorinated body extractible by ether, and a dextrorotatory strongly reducing acid. Urochloralic acid appears, therefore, to be a homologue of Jaffe's uronitrotoluic acid. J. K. C.

**Putrefaction-products of Brains.** By F. STÖCKLY (*J. pr. Chem.* [2], 24, 17—24).—A continuation of Nencki's experiments. In the author's experiments:—Bullocks' brains in portions of 1 kilo. at a time were digested, with about six times their weight of water, at 35—40° for eight days, were then acidified with acetic acid, and about one-third of the volume of the mass was distilled off.

The distillate was neutralised with sodia and extracted with ether. The ethereal residue contained skatole and paracresol.

The residue left in the retort was filtered, the filtrate concentrated to a syrup and distilled after the removal of inorganic substances. It began to pass over at 118°, the thermometer gradually rising to 200°, and then quickly to 270°; at 280° nearly all had passed over. Fraction 118—200° consists, according to the author, of all the fatty acids from acetic to caproic; this last was recognised in fraction 195—200°, by the guanidine reaction. Fraction 270—280° is hydrocinnamic acid.

By varying the time of the duration of the putrefaction, in addition to the above, succinic acid and amido-acids, principally of leucine, were found. Succinic acid is found in largest quantities after 24 hours' putrefaction, and probably owes its origin to the glycogen. The bases present have not as yet been examined by the author; he thinks the red coloration observed by Selmi on evaporating the above distillate with nitric acid is due to hydrocinnamic acid.

The scarcity of analytical data is explained by the fact that the large quantities of brains which have to be used render the separation of the bodies very troublesome. D. A. L.

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## Physiological Chemistry.

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**Effect of Feeding on the Weight of Animals.** By O. KELLNER (*Bied. Centr.*, 1881, 534—537).—For two months, two three-year-old sheep were fed on a low diet of  $1\frac{1}{4}$  kilo. hay, and at the end of that period it was found that they had lost only 1 kilo. and  $2\frac{1}{2}$  kilos. respectively. A quarter kilo. of dried hop-waste was next given in addition to 0.75 kilo. hay, and after a month their weights were not apparently altered. Finally, for three more months the above feeding was repeated, and no change was observed. Similar experiments on two-year old sheep gave somewhat similar results, and the sheep

when killed were found to be fat, and this probably in consequence of no movement being permitted during the period of experiment.

E. W. P.

**Peptone in the Blood.** By F. HOFMEISTER (*Chem. Centr.*, 1881, 506—508).—The natural occurrence of peptone in the blood is in apparent contradiction to the fact that peptone when injected produces poisoning symptoms and passes almost entirely through the kidneys into the urine. Peptone absorbed into the blood from the alimentary canal shows of course none of these symptoms, and must therefore undergo some change previous to absorption. This the author concludes can only occur in the slimy integument of the alimentary canal, where the peptone meets with lymphatic cells (colourless blood corpuscles), which, as has been previously shown, have the power of combining with it, so that it circulates in the blood without producing the effects caused by injected peptone.

J. K. C.

**Presence of Ammonia in Human Saliva.** By B. H. HEYWARD (*Chem. News*, 44, 208).—In evidence that ammonia is really present in human saliva, or at any rate, that the Nessler reaction produced is not due to any non-volatile or but slightly volatile organic base, a small quantity of saliva was placed at the bottom of a perfectly clean and dry test-tube, a little recently heated magnesium oxide was added, a slip of white filtering paper moistened with the Nessler reagent was suspended in the upper part of the tube, and this was corked and exposed to a temperature of 30°. In a few minutes the paper was rendered distinctly orange, while in a blank experiment, conducted under the same conditions, but omitting the saliva, this was not the case. It was found that most, if not all, of the ammonia came from the two principal pairs of glands, the parotid and sub-maxillary, and that of these the latter furnished notably the larger share. The quantity of ammonia present in saliva varied from 30 to 100 milligrams per litre. The author's results further show that the source of ammonia is not to be sought for in the free gas in the expired products of respiration merely condensed in aqueous solution in the mouth.

D. B.

**Amount of Cholesterin in the Human Brain.** By BENECKE (*Bied. Centr.*, 1881, 568).—The brain of a boy 15 years old contained 26.92 grams cholesterin = 2.34 per cent. The brain of a woman 19 years old contained 26.79 grams = 2.12 per cent. In four hen's eggs 0.592 gram, and in four newly hatched chickens, 0.41 gram cholesterin was found.

E. W. P.

**Decomposition of Sarcosine in the Human Body.** By J. SCHIEFFER (*Chem. Centr.*, 1881, 487—488).—According to Schultzen, sarcosine in the human organism is changed into sarcosine-sulphamic and methylhydantoic acids. The presence of the former in urine has not since been confirmed, and that of the latter was at least doubtful. Seeing that methylhydantoic acid readily changes into its anhydride, and that the latter reduces Fehling's solution, a qualitative test of the latter is easily applied, after removing all disturbing agencies. By

using this test, the author finds that the greater part of the sarcosine passes unchanged through the body, about one-fifth being converted into methylhydantoic acid, and a very small quantity into methyl urea.

J. K. C.

**Distribution of Hypoxanthine in the Animal and Vegetable Kingdom.** By A. KOSSEL (*Chem. Centr.*, 1881, 486).—The following are the percentage amounts of hypoxanthine in various animal substances. Spleen (man) 0·096, spleen (dog) 0·096; kidneys (man) 0·068, kidneys (dog) 0·053; liver (dog) 0·082; muscles (child) 0·048; heart (man) 0·039; brain (man), white matter, 0·029, grey matter 0·024. In the vegetable world it is also widely distributed, not only as the final product of molecular rearrangement, but as a component of the living tissues.

J. K. C.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Alterations in the Properties of the Nitric Ferment by Cultivation.** By R. WARINGTON (*Chem. News*, **44**, 217).—The author has shown (this Journal, **35**, 429) that ammonium chloride solution supplied with nutritive ingredients and seeded from an old solution which had previously undergone nitric fermentation, was converted into nitrous acid only. The conditions under which such a reaction takes place, are that the soil used as seed shall have undergone nitric fermentation, and shall have been kept for some months, when the ferment loses its power of converting nitrites into nitrates. Any solution which has undergone the nitrous fermentation when used as seed, produces a purely nitrous fermentation.

In ammonium chloride solution fresh soil produces purely nitric fermentation if the temperature is kept at about  $15^{\circ}$ , and the solution containing about 8 per cent.  $\text{NH}_4\text{Cl}$  is sufficiently shallow. In more concentrated solution, and at a higher temperature, nitrous acid is produced.

The diminished energy of the organism is in accordance with Pasteur's results, who finds that by allowing the cultivation of an organism to become old, an organism of diminished energy is obtained, which when cultivated continues to produce organisms of the same diminished energy.

If solutions which have been nitrified are kept for some time, a white organism not unfrequently appears on the surface, and under favourable circumstances spreads over the whole. This organism appears to consist of bacteria, and produces nitric fermentation.

L. T. O'S.

**Researches on the Physiology and Morphology of the Alcohol Ferment.** By E. C. HANSEN (*Bied. Centr.*, 1881, 558—560).—*Saccharomyces apiculatus* is an alcoholic ferment marked by a distinct form, and hence easily to be found at all times of the year. Ripe and juicy fruits are the home of this ferment, where it develops, and whence it is carried about by the wind; it is found but seldom on the ground. It is washed off by rain, or is borne to the ground by the falling fruit, where it winters, becoming active again in the following season. The ferment develops in two forms, one lemon shaped, the other more oval in outline. The first is developed soonest, but the second kind, although later, is the most abundant. *Saccharomyces apiculatus* is less energetic than *S. cerevisiæ*, for when the latter will produce 6 vol. per cent. alcohol, the former is only capable of producing 1 per cent., and beer produced by its aid is peculiar in taste and odour. It is incapable of inverting saccharose, but is very retentive of life, resisting easily all effects of temperature and moisture. In the presence of *S. cerevisiæ*, *S. apiculatus* develops the most rapidly, so much so that the action of the former is retarded.

E. W. P.

**Retardation of Fermentation by certain Substances.** By M. MÄCKER (*Bied. Centr.*, 1881, 560—562).—The presence of 0·1 per cent. of butyric acid, 0·5 per cent. acetic acid, 0·2 formic acid, 0·1 propionic acid, and a trace of caproic acid, will arrest the fermentation of sugar. The knowledge of this is important, as the first and the last acids frequently occur in the mash. Lactic acid, however, is of advantage up to 0·5 per cent., but 3·5 per cent. is prejudicial.

E. W. P.

**Composition of Cell Membranes of Bacteria.** By C. RICHTER (*Chem. Centr.*, 1881, 483).—According to Du Bary, a peculiar form of cellulose exists in the cell membranes of bacteria. If, however, the membranes are steeped in cold potash solution for a week, they then show the characteristic reactions of cellulose with iodine and sulphuric acid, and with ammoniacal cupric solution, on the absence of which reactions Du Bary grounded his theory of the existence of another kind of cellulose.

J. K. C.

**Changes accompanying the Ripening of Certain Plants.** By P. P. DÉHÉRAIN and BRÉAL (*Ann. Agronomique*, 6, 398—400).—DéhéRAIN explains the loss in weight of dry matter which occurs during the maturation of the seed in the cereals and other plants. The formation of the seed involves the transport of carbohydrates and nitrogenous bodies from one part of the plant, to be afterwards stored up in another part. In the case of the carbohydrates, this transport does not necessitate any loss in weight, since they exist in the form of reserve materials (starch, &c.), which take no active part in the phenomena of growth. But in the transport of nitrogenous bodies, a certain quantity of protoplasm has to disappear from the living cells in the form of asparagine, to reappear in the seed as legumin, gluten, &c. Assimilation then ceases in the cells thus deprived of protoplasm, but oxidation still goes on, and thus a loss of weight is produced. The authors distinguish three cases. In those plants which flower

rapidly and bear simultaneously a large number of flowers in proportion to the size of the plant (*Sinapis nigra*, *Colinsia bicolor*), there is always a loss in weight of dry matter; assimilation suddenly ceases throughout a large portion of the plant, but oxidation still goes on. In plants which do not produce many flowers at once, nor in too great proportion to the leaves, ripening is accompanied with only a temporary loss of weight; a sufficient number of chlorophyll granules remain intact to carry on the work of assimilation, which proceeds with renewed vigour after the seeds have ripened (*Escholtzia Californica*, *Delphinium ajacis*). When the flowers are very few and the leaves numerous (*Papavera somniferum*, *Hesperis maritima*, *Silene pendula*), the dry matter increases in weight during the ripening of the seed.

J. M. H. M.

**Absorptive and Diffusive Power of Leaves.** By MAQUENNE (*Ann. Agronomiques*, 6, 321—390).—In this long paper, the author describes and discusses very exhaustively the methods and apparatus employed for the determination of the absorptive and transmissive power of various substances for heat rays, and proceeds to describe in detail a great number of determinations made with different species of leaves. The general results are summed up as follows:—

1. All leaves radiate a part of the heat which they receive normal to the surface; in the case of the Bourbouze lamp (an incandescent platinum thread) the radiation is about 0.25 of the total heat; with Leslie's cube it is only a few hundredths.

2. The two sides of leaves differ in radiating power; generally the back of the leaf radiates more than the face, but sometimes the case is reversed.

3. Leaves absorb a considerable proportion of the heat emitted by the Bourbouze lamp; this absorption is due to the presence in the parenchyma of absorbent substances, such as chlorophyll and water, and to the radiation which takes place in the interior from the surface of the separate cells; the heat absorbed is generally greater for the face than for the back of the leaf.

4. Thick leaves absorb more heat than thin ones.

5. The absorptive power of leaves for the heat of boiling water is nearly the same as that of lampblack.

6. Young and thin leaves transmit more heat than thicker and older ones.

7. The radiating power of leaves is, for a slight excess of temperature, almost equal to that of lampblack; it diminishes slightly as the inclination increases.

8. The absorptive power of chlorophyll, in the mean equal to that of water for the rays of the Bourbouze lamp, increases in proportion to the distance on either side of the calorific maximum of the spectrum.

J. M. H. M.

**Analyses of Grape Juice and Unfermented and other Wines.** By J. C. BELL (*Analyst*, 6, 197—199).—The author has analysed the juice of various grapes, and finds that the total ash varies from 0.258—0.395 per cent., of which from 56.65—90.56 per cent. is soluble. In analysing the juice of grapes, it is necessary to take into consideration

the species of the grape, and the time when the juice was expressed, whether recent or old. The consideration of age does not apply in cases where the juice is mixed with large quantities of water. Analyses of "unfermented" wines show that many contain alcohol. Copious tables of results are given, for reference to which the original paper must be consulted.

L. T. O'S.

**Separation of Calcium Carbonate in the Wood of Dicotyledonous Plants.** By H. MOLISCH (*Chem. Centr.*, 1881, 483).—Separation of calcium carbonate takes place usually in the already formed wood, or in surface knots and wounds. The cells and ducts become completely filled, so that perfect castings of the interior are sometimes obtained when the wood is burnt. Deposition takes place first in the central canals, and probably on the inner surfaces of the walls; the cell-membranes are, however, not specially rich in ash.

J. K. C.

**Occurrence of Ellagic Acid in Pine-bark.** By F. STROHMER (*Monatsh. Chem.*, 2, 539—540).—Whilst trying some experiments on pine-bark tannin, the author found that ellagic acid was present, but no gallic acid. He therefore thinks that ellagic acid exists ready-formed in the bark of *Abies excelsa*.

D. A. L.

**Presence of Citric and Malic Acids in Chelidonium majus.** By L. HATTINGER (*Monatsh. Chem.*, 2, 485—490).—In 1878, O. Lietzenmayer found in this plant chelidonic acid, and an acid isomeric with malic acid. The author has repeated the experiment, and finds chelidonic, ordinary malic, and (large quantities of) citric acid. He thinks the isomeric malic acid referred to must have been a mixture of citric and phosphoric acids, for although this latter acid is present, no mention is made of it in Lietzenmayer's paper.

D. A. L.

**Contributions concerning the Phylloxera Question.** By V. MAYET and others (*Bied. Centr.*, 1881, 546—550).—V. Mayet caused galls to be produced on vines, by placing on the leaves the hatched phylloxera.

Laugier, H. Marés, and Mouillefert all speak in high terms of the success obtained by the use of potassium thiocarbonate; the latter considers that the action of this salt is greatest on sandy or clay-sandy soils. Bourden recommends that vapour of carbon bisulphide be introduced into the soil by a system of underground pipes. Macagno would treat vine-cuttings by heating them to 43° for four hours in a damp atmosphere, at which temperature the insect and its egg are rendered innocuous. He also recommends that the cuttings be placed in bundles on straw mats, in a well-closed chamber, fitted with a thermometer and manometer, and that carbon bisulphide be introduced to the amount of 250—300 grams per cm. P. Olliver finds that carbon bisulphide vapour acts harmfully on diseased, but not on healthy roots. Millardet writes concerning provining and grafting the American vines. Grafting on American stocks seems to be a preventative against the attacks of phylloxera, but mildew (*Peronospora viticola*) appears in its place.

E. W. P.

**Experiments on the Cultivation of Various Kinds of Beans, with Special Regard to the Amount of Nutrients produced.** By H. GRAHL (*Bied. Centr.*, 1881, 538—540).—The experimental plots were of two kinds, heavy and light, and were manured with 40,000 kilos. of stable manure. The plants grown were varieties of soja, French, and field beans, and the first two were not found to be greatly different in yield, whether grown on the light or on heavy land; but the field beans did the best on the heavy land. As regards the total amount of nutrients produced, it appears that the French bean is not preferable to the soja as regards protein, but is lower in fat, and its period of growth is shorter. As the black variety of French bean gave the highest yield, it is to be recommended as a fodder. The field bean is far above the soja bean in protein, but much below in fat; and the author considers that on good soils the field bean (any variety) will always yield the largest crops; but on poor soils, perhaps, by reason of the large amount of fat it contains, the soja bean ought to be grown. E. W. P.

**Employment of Soja Bean as Food for Milch Cows.** By E. BLASCOVICI (*Bied. Centr.*, 1881, 532—534).—Twenty-six cows were placed under experiment during four periods of 14 days' duration. During the first and last period the fodder consisted of chaff, sugar-beet, and hay (nutrient ratio = 1:6·3); in the second period, malt coombings; and in the third, soja beans were given. Soja beans were found to increase the yield and the quality of the milk. But the malt coombings seem to have reduced the quantity, although it raised the quality. It should be mentioned that 13 of the cows during the second period received soja bean, while the other 13 were receiving malt coombings, and during the third period the case was reversed; so that we find that soja before malt coombings in the first 13 produced a greater quantity, but that with the second 13, malt coombings before soja was most satisfactory. In both sets, the yield during the third period was lower than that during the first. E. W. P.

**Cultivation of Potatoes.** By KRIEWITZ (*Bied. Centr.*, 1881, 542).—A short statement of the yield of various kinds of potatoes grown with different manures. Peruvian guano and ammonium superphosphate seem to have been the best manures, and "Dabersche rothe" the most prolific potatoes. E. W. P.

**Amount of Non-albuminous Nitrogen in Roots.** By O. KELLNER (*Bied. Centr.*, 1881, 540).—The following figures represent the percentage of nitrogen present in the roots examined in forms other than albumin and nitric acid :—

	Grown in Lichterfelde.*	Hohenheim.	
Common beet . . . . .	60·0	54·1	
Beetroot (garden) . . . .	58·6	—	
Horse carrots . . . . .	48·1	33·0	
Kohl rabi . . . . .	42·2	39·1	
Late turnips . . . . .	—	45·3	E. W. P.

\* Grown on irrigated fields.



**Linseed Cake and Hemp Cake and their Adulteration.** By A. RENOARD and B. CORENWINDER (*Ann. Agronomiques*, 6, 414—434).—*Linseed cake*.—After some pages of remarks on the manufacture, composition, and feeding value of linseed cake, the authors describe its more common adulterations. Many buyers of this cake prefer the light-coloured samples, and to produce this appearance the manufacturers add about 20 per cent. of poppy cake. In the district of Arras and Douai, the common poppy (*Papaver somniferum*) cultivated in those parts is used; in the linseed cake imported from Holland the Indian poppy (*P. somniferum nigrum*) is found. Some merchants describe these cakes as *pavoté*. The admixture can be recognised: (1) by the bitter taste imparted to the cake; (2) by the greater fineness of grain of the adulterated cake and the absence of the reddish fragments of the episperm of the linseed; (3) by the presence of whole poppy seeds, easily seen with a magnifying lens; (4) by the density of the powdered cake, 1 hectolitre of pure linseed cake weighing 54·4 kilos., whilst 1 hectolitre of common poppy cake weighs about 68 kilos.; and (5) by extracting the oil with carbon bisulphide and adding sulphuric acid, linseed oil giving a brownish-red, almost black colour, poppy oil a dull yellow, and Indian poppy oil a slight orange. Linseed cake contains an average of 9·77 per cent. oil, poppy cake 10·19 per cent., and Indian poppy cake 7·42 per cent. Linseed cake contains 0·72 per cent. soluble salts; 6·28 per cent. insoluble; total, 7·00 per cent. Indian poppy cake contains 6·15 soluble salts; 6·22 insoluble; total, 12·37. Some samples of the latter contain as much as 16 per cent. ash.

The cake of arachida husks, being extremely cheap, is sometimes added to linseed cake; it is of no feeding value. The lens, in the hands of an expert, will detect this addition. Dust, siftings, and winnowings of various kinds are often added, but the cake so made will always differ in appearance from pure cake.

Other seeds, such as hemp, are sometimes added to linseed before expressing the oil, in order to obtain a mixed oil, a little indigo added to the mixture of linseed and hempseed oils allowing it to be sold as hempseed oil. The cake, however, cannot be sold as pure linseed cake, on account of the difference of colour. When a very little hemp cake is added to linseed cake and the product sold as pure linseed cake darkened by being kept, it is almost impossible to detect the fraud. Colza cake, the colour of which is greenish-brown, streaked with yellow, black, and red, is sometimes added in small proportion to linseed cake. It is thus detected:—Stir a little of the powdered cake with hot water in a glass, and allow to settle. If the cake is pure linseed, the liquid is divided into two layers, a blackish-brown one at the bottom, and a colourless one above. If it contains colza cake, there are three layers of liquid; the bottom one entirely black, formed of the particles of the husk of colza seed, the middle one containing a yellowish powder, and the top one a clear yellow, which disappears on the addition of a few drops of potash or soda. Rape cake, the colour of which resembles that of pure linseed, is sometimes added. Mailho's test, founded on the presence of sulphur in cruciferous seeds, may be employed to detect both rape cake and colza

cake; 25—30 grams of the oil are boiled in a porcelain capsule for some time with a solution of 2 grams of potash (purified by alcohol) in 20 c.c. water. The liquid is then filtered, and the filtrate tested with lead acetate paper. If the test is made in a silver capsule, the coloration will at once be apparent. *Potato pulp*, almost free from starch, and of no feeding value, is sometimes added, and is extremely difficult to detect. Most of the linseed cake used in France is made from seed imported from Russia and India. In former years this imported linseed often contained a large proportion of other seeds; but since the establishment of the "Linseed Association" of London, the admixture seldom exceeds 5—6 per cent. The seeds most frequently found are those of *Brassica napus præcox*, *Lolium perenne*, *Sisymbrium sphenolix*, *Spergula arvensis*, camelina, charlock, &c.

In the Département du Nord and in Belgium, many merchants sell the powdered slightly pressed linseed cake manufactured in the wind-mill factories around Lille. These cakes are often adulterated with earth, chalk, sawdust, and rice-dust. Admixture of earth of course increases the percentage of ash, but the simplest way to detect it is to plunge the naked arm into the powder, when the earth clings to the skin. Sawdust and chalk are very easily detected, but rice-dust does not alter either the appearance or taste of the powder, and animals seem very fond of it. Some of these slightly pressed cakes, when sold in the unpowdered condition, become covered after a certain time with a whitish efflorescence, and produce somnolence in animals fed with them. The whitened cakes are found to contain excess of water (14—18 per cent.), and a relatively large proportion of oil. Under these conditions the oil becomes rancid, the mucilage begins to ferment, and a growth of mould appears on the surface, forming the efflorescence. The fracture of these badly pressed cakes is not so sharp as that of ordinary cakes.

*Hemp Cake*.—This cake is used more largely as a manure than for feeding cattle. As a manure, it is said to be "hot," i.e., of rapid action, whilst linseed cake is "cold," or slow. When given to cattle, it is often slightly purgative. A recent analysis of a pure sample gave—Water, 10·00; albuminoids, 32·68; oil, 5·90; carbohydrates and fibre, 42·54; ash, 8·88; (nitrogen, 5·23). In 1869 many farmers petitioned the Government to allow the sale as manure of a mixture of oilcake and sodium nitrate, commonly known as "salts." The Government accordingly authorised the use of "salts" for this purpose free of duty, and many manufacturers have taken advantage of the decree by selling mixtures of hemp cake with *common salt*. The decree allows of any proportion up to 1,000 kilos. of salt to 200 kilos. oilcake. In consequence of animals liking the taste of these salted cakes, they are often bought by farmers in preference to pure cake.

The cake from the *Curcas bean* is very similar in appearance to hemp cake, and is often mixed with it, and sometimes whole cakes of *curcas* are sold amongst a lot of hemp cakes. The plant which produces this bean is the *Curcas purgans*, *Jatropha Curcas*, or *Jatropha cathartica*, belonging to the family Euphorbiaceæ, tribe Crotonæ, and growing especially in Central America and Cape de Verd. The oil resembles croton oil, and is used medicinally and for burning. A

single curcas seed weighed 0·721 gram, and when deprived of its husk, 0·466 gram. Analysis of the seed gave—Water, 6·390; oil, 52·780; albuminoids, 22·678; carbohydrates and fibre, 13·970; ash, 4·182. Curcas cake contains—Water, 11·50; albuminoids, 20·75; oil, 5·70; carbohydrates and fibre, 51·97; ash, 10·08; (nitrogen, 3·32). It is thus distinguishable from hemp cake by its deficiency in nitrogen, but is detected more easily, thus: Stir a little of the powdered cake in cold water and filter immediately; pure hemp cake gives an amber-coloured filtrate, but an admixture of 10 per cent. of curcas cake causes the colour to be much darker. The curcas bean is undoubtedly poisonous to animals; the meal contains *Jatrophic acid* and an acid principle called *curcasine* (Cadet). J. M. H. M.

**Digestibility of Various Oil-cakes.** By E. WOLFF and others (*Bied. Centr.*, 1881, 531).—The digestion coefficient for sheep of certain oil-cakes is as follows:—

	Protein.	Fat.	Fibre.	Extract.	Total organic matter.	Total dry matter.
Earth-nut .....	90·9	85·7	15·9	98·1	85·0	81·5
Sesamé .....	90·3	89·8	30·7	62·8	77·4	69·3
Cotton (decorticated) ..	84·7	87·6	—	95·1	80·4	74·2
Sunflower .....	89·6	87·9	30·5	77·4	75·9	69·4
Cocoa-nut .....	75·7	100·0	61·5	81·1	77·6	70·0

Earth nut cake is therefore the most digestible, but the unavoidable admixture of hairs in this cake greatly reduces its value.

E. W. P.

**Researches on the Influence exerted by the Physical Properties of a Soil on the Amount of Free Carbonic Anhydride contained in it.** By E. WOLLNY (*Bied. Centr.*, 1881, 514—516).—The factors which determine the amount of free carbonic anhydride in a soil are, temperature, water, and structure. The results of the investigation are that (1) the amount of free carbonic anhydride increases with the temperature, and (2) with the amount of water present in the soil, which has influence only so long as the air inclosed in the pores of soil does not suffer such diminution as shall render the oxygen present insufficient for the decomposition of the organic matter present; (3) if temperature and water are in inverse proportions, then the formation of carbonic anhydride is at the maximum at a definite temperature, and when a definite amount of moisture is present, while it diminishes should the temperature or the water increase. Hence (4) the influence of temperature and water on the carbonic anhydride as shown in (1) and (2), is so much the less, the drier the soil or the lower the temperature; (5) a finely-powdered condition of the soil lowers the quantity of carbonic anhydride, whilst a close heavy state raises it. E. W. P.

**Phosphoric Acid in the Soil.** By P. P. DÉHÉRAIN (*Ann. Agron.*, 6, 392—393).—Phosphatic manures are found to be of no service in the

experimental fields at Grignon, and the farmers of the neighbourhood do not employ them. The soil does not contain more than an average quantity of phosphoric acid, but from half to one-quarter of the total phosphoric acid is soluble in acetic acid, and may, therefore, be presumed to exist in the soil as calcium phosphate. It may, perhaps, be true generally, that soils which contain phosphoric acid removable by acetic acid, will not be benefited by phosphatic manures.

J. M. H. M.

**The Highest Daily Rainfall in Germany.** By H. ZIEMER (*Bied. Centr.*, 1881, 512).—The mean daily rainfall in Germany is put at too low a figure, viz., 80 mm. The rainfall of various places is quoted to show that the rainfall should be reckoned as at least 100 mm. maximum. In Kolberg 102 mm. have fallen in seven hours; at Breslau, 114·6 mm.; at Friederickshofen, 115·4 mm.; and at Klausthal, 1487 mm. have fallen in a year, making a daily maximum of 115 mm. The maximum daily rainfall of Poonah is 889 mm., and that of Katskill 487 mm. The greatest daily rainfall in Germany occurs during the months May to October, and is due to storms.

E. W. P.

**Researches on the Evaporation of Exposed Water and that in Soil, and on the Transpiration of Plants.** By F. MASURE (*Bied. Centr.*, 1881, 505—512).—Water exposed to the air in the neighbourhood of Orleans was found to have evaporated during the period August 6 to November 15, to the amount of 183 mm. The time of exposure is divided into 14 periods, and it appears that between August 12—18, a period during which the weather was remarkably warm, dry, and stormy, the evaporation reached a maximum, viz., 4·1 mm. Although the temperature may fall, yet the decrease of evaporation is not in the same ratio, as it is dependent on other factors, of which the following are the chief:—

*Influence—Morning, Evening, and Night.*—Evaporation is at a maximum in the evening, at a minimum at night, because at evening the air is warmer and drier than in the morning. At night, the amount of water evaporating is only a tenth of that which passes off during the day.

*Influence of Weather.*—As was to be expected, the amount of evaporation which took place during the periods of unclouded skies, was more than twice that which occurred when the weather was cloudy; and comparing the evaporation during the various parts of the day in the fine period with the same diurnal divisions during the cloudy or wet period, we find that the evaporation was twice as great during morning, three times as great during evening, and three times as great during the night.

*Influence of the Temperature and Hygrometric Condition of the Air.*—To estimate the influence of temperature, periods during which the hygrometric conditions were the same were compared, with the result that the higher the temperature is, so much the greater is the evaporation; and the same may be seen when the air is damp, and, conversely, when it is dry. Concerning the dew on the leaves of plants, the author considers that it is not wholly precipitated from the air, but is in part perspiration from the plant itself.

*Evaporation from the Soil.*—If the soil is very wet, so that all parts

of its surface are moist, then more water evaporates than from a like surface of water: if the soil is not excessively damp, then the evaporation is equal to that of a water-surface; if the soil is dry, then evaporation is small, the amount varying with the dryness; and these facts are dependent on mechanical, physical, and chemical causes. Firstly, capillarity hinders evaporation; the evaporation is dependent on the surface exposed by a definite area of soil; and the hygroscopic properties of certain salts reduce evaporation by retaining part of the water, and also by condensing atmospheric moisture. Soils lose more water during the morning, and less during evening and night, than free water.

*Transpiration of Plants.*—The loss of weight experienced by a plant growing in the free air can, without much error, be considered as the measure of transpiration; the true transpiration is, however, somewhat less, as the loss by carbonic acid must be taken into account before accurate determinations can be made. Experiments on immortelles show that the loss by transpiration follows the same laws as those which govern the evaporation of a like surface of water, but to a greater degree; for whereas a water-surface lost 182·32 mm., the plants lost 590·18 mm. of water. Transpiration must be considered, not as a simple evaporation, but as a definite phenomenon connected with vegetation; not only water, but nitrogen, oxygen, carbonic anhydride, and other volatile substances are transpired, and the amount of transpiration is in part dependent on the temperature, the hygrometric condition of the air, and the direct action of sunlight. Like evaporation, transpiration is greatest during the afternoon and evening, and is ten times that occurring during the night.

Sunny or bright weather, high temperature, and dry air, greatly assist transpiration.  
E. W. P.

**Passage of Rain through the Soil.** By A. AUDOYNAUD and B. CHAUZIT (*Ann. Agronomiques*, 6, 407—413).—The authors refer to a previous paper on the subject (*Ann. Agron.*, Oct., 1879). The experiments described in this paper were carried out, like the former series, in vessels of impervious cement containing a thickness of 1·5 metre of soil, the drainage-water being drawn off by a tap at the bottom. The surface of the exposed earth was 5·88 square metres. The rainfall on this surface from January 1st to March 18th, 1880, was 2,400 litres; the drainage-water collected was 500 litres, or 0·21 of the rainfall. The total solid matter removed by the water was estimated and analysed on several separate dates. The mean of all the determinations is as follows, taken from the detailed analyses given in the paper; the numbers in brackets signifying the number of determinations made of each constituent:—Total solid matter per litre, 0·861 gram (mean of 19); silica and organic matter, 0·48 (13); nitric acid, 0·032 (6); sulphuric acid, 0·143 (6); potash, 0·129 (7); lime, 0·067 (8); lime as carbonate, 0·047 (4); magnesia, 0·011 (6); chlorine, 0·237 (5); phosphoric acid and oxide of iron, traces. According to these results, the total solid matter removed from the soil per hectare per annum would be 1,300 kilos., assuming a rainfall of 0·75 metre, and that 20 per cent. of this passed through the soil. On three occa-

sions, the residue was analysed with a view to obtaining its proximate composition. The results for February 27 are as follow:—Silica and organic matter, 0·003; carbonate of lime, 0·073; other earthy carbonates, 0·051 (= 0·156 insoluble in water); potassium sulphate, 0·192; calcium sulphate, 0·048; magnesium sulphate, 0·024 (= total sulphates, 0·264); potassium nitrate, 0·047; sodium chloride, 0·377; total solid matter, 0·844 gram per litre.

The quantity of nitric acid in the drainage-water varies very much with the previous rainfall, being greatest after a spell of dry weather. Adopting 0·022 gram per litre as the average, it would amount to 33 kilos. of nitric acid removed per hectare per annum. It is, however, probable that more than this amount is yearly carried down into the soil by rain. The potash removed per annum amounts to about  $\frac{1}{2\frac{1}{4}}$  of that contained in the soil. Although only a trace of phosphoric acid was dissolved by the drainage-water, the soil was capable of growing a good crop of wheat. J. M. H. M.

**Mode of Optically Demonstrating the Permeability of a Soil for Air.** By J. SOYKA (*Chem. Centr.*, 1881, 427—430).—The formation of carbonic anhydride and nitric acid is said to be intimately connected with the different volume and size of the pores in the soil. The exhalation of a soil and its permeability for water and property of conducting heat also depend on the constitution of the pores. Mayer has shown that the essential differences in the porosity of a soil consist not so much in the total quantity of pores present as in their size and width, and that the absorptive power of a soil for water depends largely on this circumstance. The same applies to the absorptive power of a soil for air.

Renk has made a series of experiments with a view of ascertaining the permeability of several soils for air by measuring the quantity of the latter when forced through soil in a given time and at a determinate pressure.

The author proposes to pass gas through the soil, so that on its efflux it can be collected and burnt. He has constructed an apparatus to demonstrate this effect optically. As the permeability of a soil for air is greater, so the quantity of gas which passes through the soil at a certain time and pressure is greater, the gas when burnt exhibiting a larger and more luminous flame. D. B.

**Manuring Experiments at the Experimental Station at Göttingen.** By G. DRECHSLER (*Bied. Centr.*, 1881, 524—531).—The experiments on sugar-beet herein described were made during the years 1877—80, and were a continuation of those before described (*Abstr.*, 1881, 922), whereby it was hoped to determine the corrections to be applied to field experiments. In 1877 the effect of a double supply of Chili saltpetre in conjunction with superphosphate was tried, and it was found that the increased supply of nitrogen thus given produced no marked effect, and that the unmanured plots gave a higher yield than those manured with superphosphate. The reason of these results cannot be correctly explained, and no duplicate experiments existed to control the results of the originals. In another

series of experiments, the double supply of nitrogen produced the highest yield, and the single supply a higher yield than the simple phosphoric acid manuring. But still the unmanured plot was found to have produced more than some of those which had been manured.

The experiments of 1879 were also uncertain as regards the conclusions to be drawn from them. The author attempts to introduce a correction, and calculates from the actual what the true yield should be. This calculation is rendered necessary by reason of the failure of some of the roots. The weight of the missing roots is considered to be three-fourths of the mean weight of the roots actually harvested, and this figure is then added to that representing the weight of the crop. On the whole, in this year, manuring increased the yield considerably, but the quantity of sugar was not increased, in fact excess of nitrogen decreased its percentage in the juice.

In 1880 the variations in yield of one plot from the other, when manured alike, were so different, even when the correction was applied, that but little reliance can be placed on the results. This variation was most probably due to differences in the soil, and also to external influences on the growth of the roots, which influences produced a greater effect than the manures.

However, taking the results as they stand, precipitated phosphate seems to have been the most beneficial, and the amount of sugar does not appear to be affected. According to the author, all experiments with roots, in which the roots are small, and the numbers contained in the plots differ widely, even after application of a correction, are to be considered as failures. Tollens, who made the sugar analyses of the above roots, considers that manuring has no direct influence on the amount of sugar, but that nitrogenous manures cause the roots to be large and strong.

E. W. P.

**Comparison of Fine-grained with Coarse-grained Superphosphate.** By F. FARSKY (*Bied. Centr.*, 1881, 565).—Fine-grained superphosphate contains less soluble phosphate than coarse-grained, therefore unequally grained superphosphates must be well mixed to produce good results. Also the fine grained loses its soluble phosphate most easily, becoming "reduced." To obtain the best results with this last, it must be thickly spread, and causes the sprouting of the grain to be more regular, and is best adapted for such seeds as are to be thickly sown; it should be put in with the seed, or else much phosphoric acid is lost.

The coarse-grained may be used when the sowing is wide.

E. W. P.

**Results of Experiments on the Relative Value of Soluble and Insoluble Phosphates.** (*Bied. Centr.*, 1881, 518).—The experiments undertaken by the Rochester Farmers' Club on a two feet deep sandy loam (subsoil chalk) containing  $N = 0.21$ ,  $K_2O = 0.08$ ,  $P_2O_5 = 0.12$  per cent., were made with the object of testing the value of various forms of superphosphate as compared with insoluble phosphate, on the growth of swedes. The maximum yield was obtained by the use of dissolved bones, the minimum by the use of finely powdered

raw bones. Several of the manured plots are below the unmanured plot in yield. E. W. P.

**Experiments on the Application of Various Phosphates as Manure for Swedes.** By J. W. KIMBER (*Bied. Centr.*, 1881, 519—521).—Bone-meal, dissolved coprolite, coprolite powder, precipitated phosphate, &c., were applied in equal money value as manures on plots  $\frac{1}{20}$  acre; dissolved bones produced the best, and powdered phosphorite the worst crop. That coprolite powder produced a better crop than bone-meal is explained by the fact that the latter being very light, great difficulty was experienced in introducing it evenly into the heavy soil. The precipitated phosphate was heavy and lumpy, and therefore it was less active than superphosphate or dissolved bones. E. W. P.

**Experiments on Turnips with Soluble and Insoluble Phosphates.** By E. W. PREVOST (*Bied. Centr.*, 1881, 516—518).—The experiments made on soil containing 9·4 per cent. chalk were divided into two sets. In the one superphosphate and insoluble phosphate, finely ground, were applied in such quantities that the roots should receive equal amounts of phosphoric anhydride, taking 3 cwt. of 27·6 per cent. superphosphate as the basis; in the second series, equal quantities as regards money value were applied, again taking 3 cwt. superphosphate as basis. The plots were  $\frac{1}{80}$  acre, and were in triplicate in both cases, the roots being drilled in in four rows.

Taking the average yield of the crops, the following were the results:—When the manures were applied in quantities containing equivalent amounts of phosphoric acid, the increase in yield over the unmanured plots was, in the case of insoluble phosphate, about 18 per cent., in the case of superphosphate about 29 per cent. When the quantities of manures added were of equal money value, then the increase over the unmanured plots was respectively 30 and 53 per cent. Analyses of the roots showed that those grown under the influence of the insoluble phosphate, although smaller, contained less water and more sugar than those grown with superphosphate. A theoretical calculation of the feeding values of the crops, after deduction of the expenses of manures, is made, whereby it is shown that the crop grown with insoluble phosphate is of an absolutely higher value than that given with superphosphate. E. W. P.

**Comparative Value of “Reduced” and “Soluble” Phosphoric Acid in Superphosphates.** By M. MÄRKER (*Chem. Centr.*, 1881, 446).—*Precipitated Calcium Phosphate.*—In reference to the yield of corn and production of straw, this is equal in manurial value to superphosphates with an equal quantity of soluble phosphoric acid. Potatoes and other fleshy roots, however, give the largest yield with superphosphates.

*Kladnophosphate.*—The preceding applies also to this manure.

*Superphosphates prepared from Lahn Phosphorites with “Reduced” Phosphoric Acid.*—In some cases these superphosphates have been as



effective as soluble superphosphates; they are, however, inferior in value to the above phosphates.

*Half phosphates* containing exclusively dicalcium phosphate cannot be prepared by decomposing with a minimum quantity of sulphuric acid, which only partially converts the basic calcium phosphate into soluble phosphoric acid, leaving the remainder unaltered. At times, however, half phosphates have compared favourably with soluble superphosphate, a circumstance which proves that a smaller addition of phosphoric acid would often have given equally good results.

D. B.

**Phosphorite as a Manure.** By L. SIEGFRIED (*Bied. Centr.*, 1881, 566).—Osteolite and phosphorite from Edelsberg, of a light colour, and almost free from iron, alumina, and magnesia, are easily decomposed, and are therefore well adapted for composting. The value of tricalcium phosphate in phosphorite is about a halfpenny a pound, whereas that in steamed bone-meal about  $1\frac{1}{4}d.$ , when the nitrogen is taken into account, but otherwise it is to be reckoned at  $4d.$

E. W. P.

**Manuring with Kainite.** By H. G. (*Bied. Centr.*, 1881, 568).—Kainite, by destroying the caterpillars, proved itself a good manure for meadow lands, especially as regards the clovers. It seems also to be harmful to snails and worms.

E. W. P.

**Manures.** By M. SERRET (*Ann. Agronomiques*, 6, 391—392).—Some years ago Serret applied a large quantity of sodium nitrate to a pasture. The hay crop was magnificent, but the animals fed, on it suffered much from thirst, excess of urine, &c. Since then, he has used chemical manures only in admixtures with vegetable compost, with good results. He adheres to Liebig's proposition, that everything constituent to the plant should be returned to the soil. J. M. H. M.

**Value of the Waters of the Isère and Durance for Agricultural Purposes.** By DE GASPARIN (*Compt. rend.*, 93, 453—455).—The following table gives the amount of the principal constituents in parts per million:—

	Isère.		Durance.	
	I.	II.	III.	IV.
Sulphuric acid . . . .	26·8	50·9	47·9	86·4
Carbonic acid . . . . .	77·3	102·2	101·0	101·2
Hydrochloric acid . .	—	14·5	12·3	14·3
Lime . . . . .	50·9	75·0	79·6	90·9
Magnesia . . . . .	10·9	21·0	13·0	24·3
Soda . . . . .	—	12·4	10·5	12·2
	165·9	276·0	264·3	329·3

Sample No. 1 was taken in June, 1881, when the river was swollen by the melting of the snows; No. 2 in August, when the river was very low; No. 3 in July, 1881, when the river was full; and No. 4 in December, 1879. In June, 1881, the Isère contained 1 gram of suspended matter

per litre; in August it contained 2 grams per litre. The composition of the suspended matter in both rivers is given in the following table:—

	Isère.	Durance.
Insoluble residue .....	57·600	47·280
Calcium carbonate .....	30·410	42·580
Magnesium carbonate ....	1·710	1·040
Potash .....	0·055	0·072
Ferric oxide .....	5·980	5·925
Alumina.....	2·330	1·489
Combined water, organic matter, &c. ....	1·915	1·614
	<hr/> 100·00	<hr/> 100·00

The argillaceous and calcareous character of the suspended matter renders the water of both rivers suitable for the irrigation of light and gravelly soils. Both rivers are, from an agricultural point of view, deficient in organic matter.

C. H. B.

**Manuring of Fruit Trees.** By NOACK-BESSUNGEN (*Bied. Centr.*, 1881, 568).—Manure should be applied to fruit trees during the period of active growth, in the liquid form. Nitrogenous manures are requisite for backward, but potash and phosphoric acid for forward trees, as the first class of manures aids the growth of the tree, the last, the bloom, the sugar in the fruit, and the ripening of the wood.

E. W. P.

**Manuring of Potatoes and Sugar-Beet.** By E. WILDT (*Bied. Centr.*, 1881, 521—524).—It was considered that the quantities of phosphoric acid and nitrogen (*viz.*, 20 kilos. and 7·5 kilos. per morgen), stated by Märcker to be necessary for the above crops, are too great. Therefore in Posen, at seven stations, experiments were instituted, using only 10 kilos. soluble phosphate and 5 kilos. nitrogen; 100 centners of stable manure was also employed. Generally speaking, the action of the artificial manures, compared with that of stable manure, was too low, and from the tables representing the yields at the various stations we may conclude that on the whole in Posen 10 kilos. phosphoric acid with 5 kilos. nitrogen, or 100 centners stable manure together with 10 kilos. phosphoric acid, are sufficient to produce a satisfactory yield of potatoes; and that for beet the best mixture consists of 20 kilos. phosphoric acid and 10 kilos. nitrogen.

E. W. P.

**Employment of Box-Trees in Agriculture.** By J. PIERRE and T. SERANE (*Bied. Centr.*, 1881, 569).—Box-trees, as they contain in the green state 1·17 per cent. nitrogen, whilst stable manure contains only 0·41, are recommended as a manure, and the twigs of this tree can be used as a litter in conjunction with straw.

E. W. P.

**Preparation of "Manure-meal."** (*Bied. Centr.*, 1881, 566).—A short description of the process employed for converting fat and bones into a manure by the Liebig's Extract of Meat Company. The

manure contains 7—9 per cent. moisture, 5·5—7·5 N, 12—17 per cent.  $P_2O_5$ , and the output is about 30,000 kilos. daily. Flesh-meal, from the residues from the meat-extract process, and to which sodium phosphate and potassium chloride are added, contains 7—9 per cent. water, 13 per cent. nitrogen, 11—14 per cent. fat, and 5 per cent. ash.

E. W. P.

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## Analytical Chemistry.

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**Estimation of Chlorate in Hypochlorites.** By E. DREYFUS (*Bull. Soc. Chim.* [2], **36**, 202—205).—This method is based on the fact that stannous chloride reduces a boiling acid solution of cupric chloride to cuprous chloride, the reduction being complete when the liquid becomes colourless. The solutions required are (1) a solution of copper sulphate, containing 39—40 grams per litre; (2) an acid solution of stannous chloride, prepared by dissolving 15 grams in 200 c.c. hydrochloric acid, and diluting to 1 litre; (3) a solution of 5.917 grams potassium chlorate in 1 litre of water (1 c.c. = 0.005 calcium chlorate). To determine the relation between the copper solution and the solution of the chlorate, 10 c.c. of the former are placed in a flask, mixed with 50 c.c. pure hydrochloric acid, heated to boiling, and stannous chloride then added, until the solution is just decolorised. To the colourless liquid 5 c.c. of the chlorate solution are then added, and the amount of copper oxidised determined by means of the stannous chloride. The relation between the copper and potassium chlorate solutions should be redetermined from time to time.

10 grams of bleaching powder are suspended in 100 c.c. of water, and a slight excess of ammonia gradually added. The liquid is then boiled to expel excess of ammonia, transferred to a 250 c.c. flask, and the precipitate allowed to settle. The addition of a small quantity of potash to the ammoniacal liquid causes the precipitate to settle much more rapidly. 10 c.c. of the copper solution are mixed with 50 c.c. hydrochloric acid, heated to boiling, and decolorised by addition of stannous chloride; 50 c.c. of the clear solution to be tested are then added, the liquid again boiled and titrated with stannous chloride. From the numbers thus obtained, the amount of calcium chlorate in the bleaching powder can be readily calculated. This process is equally applicable to solutions of hypochlorites. C. H. B.

**Volumetric Estimation of Phosphoric Acid.** By E. PERROT (*Compt. rend.*, **93**, 495—496).—Two solutions are prepared, one by dissolving 6.85 grams silver nitrate in a litre of water, and the other by dissolving 5.414 grams pure sodium chloride in two litres of water. The insoluble phosphate is treated with nitric acid of sp. gr. 1.030, and the solution filtered from insoluble matter. The filtrate is then rendered alkaline with ammonia, the precipitated phosphates are filtered off, carefully washed, and then treated with acetic acid, which dis-

solves only the calcium and magnesium phosphates. The insoluble iron and aluminium phosphates are washed with dilute acetic acid, and ammonia is added to the solution of calcium and magnesium phosphates, until a slight permanent precipitate is formed; this is dissolved by addition of a drop of acetic acid, and 100 c.c. of the silver solution are run in from a pipette. The precipitate of silver phosphate is then allowed to settle, and the excess of silver solution determined by means of the solution of sodium chloride. To estimate soluble phosphates, the mineral is treated with water, without the addition of acid. Retrograde phosphoric acid is dissolved by means of citric acid in the usual way.

C. H. B.

**Sodium Cobalt Nitrite as a Test for Potassium.** By C. O. CURTMAN (*Ber.*, 14, 1951—1952).—The dark purple solution which is formed when cobalt nitrate\* is dissolved in a saturated solution of sodium nitrite (10 parts), slightly acidified with acetic acid, yields an immediate yellow precipitate with concentrated solutions of potassium, ammonium, rubidium, and caesium. The presence of lithium, barium, calcium, or strontium salts does not interfere with the reaction. Potassium iodide must be removed, if it is present.

W. C. W.

**Estimation of Potassium in Potassium Salts and in Manures.**

By A. ROUSSELOT (*Bull. Soc. Chim.* [2], 36, 200—202).—Dissolve 10 grams of the substance in a litre of water; if the potassium is present as sulphate, take 125 c.c. of this, or if as chloride, nitrate, &c., 250 c.c.; boil for some minutes, and add 20 c.c. or if the potassium exists as sulphate, 50 c.c. of a 5 per cent. solution of baryta. Then pass a current of carbonic anhydride into the liquid, boil for half-an-hour, and allow to stand for some time. Filter, wash, and dilute the filtrate to 500 c.c. To determine the potassium, if present as sulphate, take 200 c.c. of the original solution; or if present as chloride, &c., 100 c.c.; add 40 c.c. of a 10 per cent. solution of platinum tetrachloride, evaporate to dryness on a water-bath, take up with alcohol of 60°, containing 10 per cent. of ether, and wash the precipitate with the same liquid. This mixture of alcohol and ether may be replaced by a saturated aqueous solution of potassium platinochloride. The precipitated platinochloride is dissolved in hot water, and the boiling solution poured into a porcelain dish containing a boiling solution of 2 grams sodium formate, in 500 c.c. of water. Boil for 15 minutes, wash the precipitated platinum first with dilute hydrochloric acid, then with water, ignite and weigh.

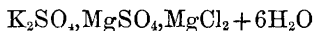
To apply this method in the analysis of manures, extract 10 grams of the latter completely with water, filter, and make up to 1 litre. Take out a quantity corresponding with 1.25—5 grams of the manure, add baryta-water, boil for at least 30 minutes, in order to expel all the ammonia, and completely precipitate the phosphoric and sulphuric acids, then pass a current of carbonic anhydride into the liquid, and proceed as above.

C. H. B.

\* The use of sodium cobalt nitrite as a reagent for potassium has already been suggested by L. de Koninck (*Zeits. Anal. Chem.*, 1881, 390).

**Analysis of Commercial Potassium Iodide.** By O. KASPAR (*Analyst*, 6, 203).—A normal solution of mercuric chloride is prepared by dissolving 2.71 grams  $\text{HgCl}_2$  in cold water (1 c.c. = 0.06643 gram KI). 10 grams potassium iodide are dissolved in 50 c.c. water, and to 5 c.c. of this solution the mercuric chloride is added until a permanent reddish-yellow opalescence appears, at which point all the iodide is converted into the double mercuric potassium iodide,  $\text{HgCl}_2 + 4\text{KI} = \text{HgI}_2 \cdot 2\text{KI} + 2\text{KCl}$ . It is advisable to prepare the mercuric chloride solution as it is required.  
L. T. O'S.

**Determination of Potassium Sulphate in Kainite.** By H. PRECHT (*Chem. Centr.*, 1881, 201).—The author makes use of the circumstance that kainite occurs in mines in conjunction with rock-salt, the quantity of the latter varying considerably, whereas the quantity of anhydride and alumina is the same in different layers of the rock. As kainite corresponding with the formula



contains 14.28 per cent. chlorine, and 60.61 per cent. when associated with rock-salt, this difference affords a means of ascertaining with accuracy the amount of potassium sulphate. An increase of 1 per cent. in chlorine decreases the quantity of potassium sulphate by 0.76 per cent., the sodium chloride is simultaneously increased 2.16 per cent. The chlorine is determined volumetrically, and if kainite is free from carnallite very accurate results may be obtained, agreeing within 0.3 per cent. or less with the determination of potassium sulphate by precipitation as platinum salt.  
D. B.

**Plastering of Wine.** By JAY (*Bied. Centr.*, 1881, 574).—To determine the extent of "plastering" which the wine has undergone, and which is permitted only to the extent that not more than 2 grams potassium sulphate shall be contained in the litre, 5.9695 grams barium chloride are dissolved in 900 c.c. water, and 20 c.c. concentrated hydrochloric acid having been added, the whole is made up to a litre. 20 c.c. of this solution are equivalent to 2 grams  $\text{K}_2\text{SO}_4$  per litre when 50 c.c. of the wine are employed. If on the addition of 20 c.c. barium solution to 50 c.c. of wine the whole of the sulphate is not precipitated, then the wine is to be rejected.  
E. W. P.

**Determination of Alum and Gypsum in Wine.** By LOUVET (*Chem. Centr.*, 1881, 252).—200 c.c. wine are evaporated to dryness, incinerated and ignited, and the ash is fused in a platinum crucible with 3 grams sodium carbonate, whereby the lime, magnesia, and ferric oxide are converted into insoluble carbonates. The mass is dissolved in water and the solution filtered. As the solution may contain sodium aluminate, it is acidified with hydrochloric acid, treated with a large excess of sodium carbonate, and the alumina collected on a tared filter. The filtrate contains all the alkaline bases. The insoluble portion of the fused mass containing the chief portion of the aluminium is fused with a few grams of pure soda, and the fused product digested several times with water. The solutions are mixed

together, and treated for aluminium as above mentioned. The precipitate is collected on the tared filter previously used, after being washed several times with distilled water by decantation. It is then dried, ignited, and weighed. In order to determine gypsum in wine, Marty ignites the evaporated residue, and treats the ash with very dilute nitric acid. The mixture is then filtered, precipitated with barium chloride, and weighed as barium sulphate. D. B.

**Precipitation of Barium Sulphate.** By T. O C. SLOANE (*Chem. News*, 44, 221).—To insure the formation of a precipitate which will not pass through the filter-paper when sulphuric acid is precipitated as barium sulphate, the solution should be barely acid, and at nearly boiling heat. The precipitate is often discoloured by the presence of iron, from which it is freed by allowing the precipitate to settle, decanting the clear supernatant solution, boiling the precipitate with 5–10 c.c. hydrochloric acid, neutralising with ammonia, and acidifying. A perfectly white precipitate free from iron is thus obtained.

L. T. O'S.

**Separation of Magnesium from Calcium, Iron, and Alkalis.** By H. HAGER (*Chem. Centr.*, 1881, 468–469).—Magnesium oxalate is soluble in oxalic acid in the cold, and does not separate out at all if the solution is mixed with glycerol, but is precipitated completely on boiling for five minutes. Advantage is taken of this fact to separate magnesium from other metals. If calcium is present, both metals existing as carbonates, the finely-powdered sample is mixed with ten times its weight of glycerol and a little water, and then with excess of a 5 per cent. solution of oxalic acid: after standing for half an hour, the mixture is filtered from insoluble calcium oxalate, which is washed and weighed: the filtrate is boiled for ten minutes and then filtered hot, and the magnesium oxalate collected and washed. Both the oxalates may of course be converted into oxides before weighing. Should the calcium and magnesium be present at first in solution, this is to be mixed with glycerol after neutralisation, and treated with ammonium oxalate and oxalic acid to strongly acid reaction, the process being then carried out as before. To separate magnesium from iron, both being in solution as salts, the liquid is treated with glycerol, then with excess of ammonium oxalate and oxalic acid; after boiling and separating the magnesium oxalate, the filtrate is boiled with excess of ammonium carbonate, evaporated, and the glycerol taken up with alcohol, the insoluble ferric hydrate being then washed and weighed in the ordinary way.

J. K. C.

**Separation of Cadmium and Zinc.** By KUPFFERSCHLAGER (*Chem. Centr.*, 1881, 470).—A polished zinc plate is introduced into the neutral solution of the two metals, and allowed to remain until the whole of the cadmium is precipitated; it can then be filtered off and weighed, the loss of weight undergone by the zinc plate serving as control.

J. K. C.

**Determination and Separation of Metals.** By BEILSTEIN and L. JAWEIN (*Chem. Centr.*, 1881, 251).—I. *Direct Separation of Man-*  
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*ganese from Iron.*—The authors recommend the following methods:—  
1. The first method depends on the fact that iodine precipitates the whole of the manganese from a solution of potassium manganicyanide in the cold, whilst iron is not precipitated from the analogous compound. 2. The second method is based on the property which manganese salts possess of being precipitated as  $MnO_2$  when heated with nitric acid and potassium chlorate.

II. *Quantitative Determination of Zinc.*—The solution of zinc acidified with nitric or sulphuric acid is treated with soda until the commencement of the precipitation; potassium cyanide is then added until the solution becomes clear, and platinum electrodes connected with four Bunsen cells are placed into the solution. After precipitation the electrode is taken out, the zinc washed with water, then with alcohol, and finally with ether. It is then dried over sulphuric acid, weighed, and the zinc is dissolved in hydrochloric and nitric acids. The electrode is again placed in the solution, in order to secure the complete precipitation of the zinc.

III. *Quantitative Determination of Cadmium.*—The nitric acid solution of cadmium is neutralised with potash, and potassium cyanide is added until the precipitate first formed is redissolved. The vessel containing the solution is then placed into cold water, and the electrodes are introduced, the decomposing cell being covered with a glass cover.

The authors use three Bunsen cells. The cadmium deposited at the cathode is washed with water, then with alcohol, and finally dried. D. B.

**Estimation of Ferrous Oxide in the presence of Ferric Oxide, Organic Acids, and Sugar.** By J. M. EDER (*Chem. Centr.*, 1881, 469).—This method depends on the fact that potassio-ferrous oxalate precipitates metallic silver from a solution of the nitrate, being converted into ferric salt in presence of a sufficient quantity of silver nitrate; when the solution contains tartaric acid the precipitated silver is free from oxalate, and can be at once weighed. The process is carried out as follows:—The feebly acid liquid is treated with excess of neutral potassium oxalate, and then with excess of silver nitrate. After a few minutes, tartaric acid is added to prevent the precipitation of ferric oxide by ammonia, and then excess of ammonia with a little ammonium chloride. The latter serves to cause the precipitated silver to flake together; the silver is then washed with ammonia and ammonium chloride and weighed. The presence of chlorides does not affect the result so long as silver nitrate is added in excess. J. K. C.

**Colorimetric Estimation of Carbon in Iron.** By EGGERTZ (*Chem. News*, **44**, 173—176).—An accuracy of nearly 0.01 per cent. being now required in the estimation of carbon in iron, greater attention must be paid to the details of the colorimetric process. The nitric acid and water used should be entirely free from chlorine; to 0.1 gram iron containing a lower amount of carbon than 0.25 per cent., add 2.5 c.c. nitric acid; with carbon of 0.3 per cent. use 3 c.c.,



with carbon 0.5 per cent. use 3.5 c.c., and for carbon 0.8 per cent. use 4 c.c. nitric acid. For steel with a greater amount of carbon take 5 c.c. nitric acid, as also for white cast-iron, but only 0.05 gram of it should be weighed with great accuracy. For normal solutions, use mixtures of chlorides of iron, copper, and cobalt in hydrochloric acid, and diluted to the standard strengths required: these solutions are quite permanent. The size of the measuring tubes, condition of the light, addition of equal volumes of water, &c., are points which of course must be carefully attended to, when great accuracy is required. Experiments with manganese, copper, phosphorus, silicon, and sulphur showed that the presence of these bodies in iron does not affect the result.

J. K. C.

**Use of Bromine in the Analysis of Nickel and Cobalt.** By G. LANGBEIN (*Chem. Centr.*, 1881, 470).—In the course of analysis, when the sulphides of nickel and cobalt are on the filter together, they are best dissolved by a solution of bromine in hydrochloric acid, which is kept in contact with the sulphides by a contrivance for stopping up the neck of the funnel.

J. K. C.

**Lead in Potassium Bromide.** (*Analyst*, 6, 203).—The presence of lead in potassium bromide may be detected by means of ammonium sulphide. Sulphuric acid cannot be used, since lead sulphate is soluble in potassium bromide.

L. T. O'S.

**Estimation of Red Lead.** By H. FLECK (*Chem. Centr.*, 1881, 252).—The method consists in heating a weighed quantity of the sample with dilute hydrochloric acid and passing the chlorine gas evolved into a solution of potassium iodide; the iodine which is separated is titrated with sodium thiosulphate.

D. B.

**Quick Method for the Estimation of Lead in Tin.** By ROUX (*Chem. Centr.*, 1881, 470).—The alloy is decomposed with nitric acid, treated with sodium acetate, and the tin dioxide filtered off. The filtrate is cautiously precipitated with a standard solution of potassium dichromate, and the excess estimated by means of a standard solution of ammonio-ferrous sulphate, potassium ferrocyanide being used as indicator.

J. K. C.

**Estimation of Arsenic.** By H. HAGER (*Chem. Centr.*, 1881, 465).—Hager claims priority in the suggestion of adding ferrous chloride to the solution of a substance to be examined for arsenic, when the latter is to be estimated by Schneider's method, and is in the form of pentoxide.

J. K. C.

**Detection of Mercury in Animal Substances.** By E. LUDWIG (*Chem. Centr.*, 1881, 202).—The author has modified his original method of detecting mercury in urine and other animal substances

(*Wien. Med. Jahrb.*, 1877, 143). In the original process the substance containing the mercury is mixed with finely-divided zinc-dust or copper, and the mercury distilled off in a glass tube; it condenses in the capillary part of the tube along with water. When the capillary tube becomes full, it frequently happens that the water is forced out of the tube, and with it the mercury. Hence the author now uses a tube closed at one end and narrowed at the other. The vapours pass over a layer of well-dried zinc-dust before reaching the capillary part of the tube, thus the vapours of water are decomposed and mercury only condenses in the capillary end. The evolution of gas dependent on the presence of moisture, and the dry distillation of the organic substance, suffice to carry the greater portion of the mercury into the capillary tube, so that it is not necessary to use an aspirator.

D. B.

**Williams's Nitrogen Process.** By T. P. BLUNT (*Analyst*, 6, 202).—Accurate results may be obtained in the case of any water by using Williams's zinc-couple process without distillation, by adding oxalic acid to a double quantity of the water, dividing, and using one portion cleansed by standing in a stoppered bottle, as a comparison liquid for testing against the other treated with zinc-couple in the usual manner. By this modification, an equal turbidity is obtained in each case, and any ammonia which the oxalic acid may contain does not interfere with the result.

L. T. O'S.

**Separation of Nitrous and Nitric Acid from the Living Organism.** By F. RÖHMANN (*Chem. Centr.*, 1881, 485—486).—From a series of experiments with dogs and rabbits, it was found that a separation of nitrates and nitrites in the urine could be traced to the presence of nitrates in the food, and was not the result of any part of the digestive process. The reduction of nitrates to nitrites and ammonium salts was observed in several cases.

J. K. C.

**Relative Proportions of Olefines in Shale and Petroleum Products.** By A. A. ALLEN (*Analyst*, 6, 177—180).—To estimate the proportion of olefines to paraffins in the products obtained from shale and petroleum, the olefines were converted into dibromides by treatment with sodium hypobromite and hydrochloric acid.

A solution of sodium hypobromite is prepared by gradually adding soda to 40 c.c. of bromine (avoiding any rise in temperature) until the liquid is slightly alkaline and of a pale-yellow colour, and diluting the solution to 1 litre. The hypobromite in this solution is estimated by Bunsen's method for the estimation of bleaching-powder.

To determine the amount of olefine present in the product, 5 c.c. or 5 grams of the oil are treated with the hypobromite and excess of hydrochloric acid in a separating funnel, and after well shaking, the layer, which must be of a permanent red colour, is separated and shaken with soda until colourless. This solution is separated, the oil washed with water, and the washing added to the alkaline solution, in which the bromine is estimated by means of potassium iodide and

sodium thiosulphate. The difference between this amount and that originally added to the oil gives the amount of bromine taken up by the unsaturated hydrocarbons. In the case of solid hydrocarbons, 2 grams are dissolved in the smallest quantity of light petroleum, which has been previously shaken with bromine and soda. In some cases, to effect the complete separation of the oil from the hypobromite solution, it is necessary to add sufficient light petroleum (previously treated) to enable the oil to rise readily to the surface.

The absolute amount of olefines present cannot be obtained by this method, owing to the complex nature of the hydrocarbon, but their relative amounts in different oils, in terms of bromine, is shown in the following tables:—

Substance.	Sp. gr. at 15·5° C.	Grams bromine com- bining with 100 grams substance.	Percentage of Br in product.
<i>Naphthas.</i>			
1. Gasolene from shale .....	0·665	67·1	41·6
2. Gasolene from petroleum .....	0·652	5·1	4·8
3. Shale naphtha .....	0·718	94·9	48·7
4. Petroleum naphtha .....	0·690	10·0	8·8
5. Benzol .....	0·876	36·2	26·6
<i>Burning Oils.</i>			
6. From shale .....	0·801	38·7	27·9
7. Ditto .....	0·806	36·4	26·7
8. From petroleum .....	0·800	17·2	14·7
<i>Lubricating Oils.</i>			
9. From shale .....	0·889	56·4	36·0
10. Ditto (bloomless) .....	0·875	45·3	31·2
11. From petroleum (spindle valvoline) .....	0·862	21·6	17·7
12. Ditto (oleo naphtha) .....	0·905	31·8	24·1
13. Resin oil .....	0·973	45·3	31·2
14. Refined resin oil .....	0·978	42·7	29·9
<i>Solid Products.</i>			
15. Vasilin .....	—	19·7	16·5
16. Paraffin wax .....	—	—	—

From these results it is seen that the amount of bromine taken up by the oils from shale is much in excess of that taken up by the corresponding petroleum product; generally from twice to ten times as much assuming that all the brominated product consists of brominated olefines. The amount of hydrocarbon may be roughly estimated by taking the vapour-density of a fraction of constant boiling point, and regarding the result as the mean vapour-density.

Benzene does not yield satisfactory results, since the reaction takes place but slowly.

L. T. O'S.

**Decomposition of Cyanides.** By VAN DER BURG (*Chem. Centr.*, 1881, 466).—The method of separating easily decomposable cyanides from stable cyanides such as those of silver and mercury, ferrocyanides, &c., by the addition of an acid and passing a stream of air through them into potash-solution, does not work well when only small quantities of the former are present, as ferrocyanides are slightly decomposed under this treatment; moreover, a stream of air alone will expel small quantities of hydrocyanic acid from solutions of alkaline cyanides.

J. K. C.

**Composition and Examination of Rum.** By H. BECKURTS (*Arch. Pharm.* [3], 18, 342—346).—Rum is the product obtained by distilling fermented molasses; it is at first colourless, but acquires a brown colour on standing in casks. Artificial rums are produced by colouring spirits of wine with burnt sugar and flavouring with ethyl acetate and butyrate, essence of violets, infusion of raisins and locusts; extract of oak bark and tincture of catechu are often added. A rum-essence is also sold which, added to spirits of wine, produces an artificial rum without any further addition. Such an essence is produced by distilling a mixture of 75 kilos. of alcohol (90 per cent. by vol.), 50 kilos. of wood vinegar, 30 kilos. of sulphuric acid, 20 kilos. of manganese dioxide, and 10 kilos. of potato-starch, colouring the distillate brown with burnt sugar. The most important constituents besides alcohol are the ethyl compounds of various organic acids, especially formic acid.

It is difficult to distinguish chemically between genuine and artificial rum, especially as extractive matter is generally if not always added to the genuine product at the place of its manufacture. The author examined various samples of rum with the following results; the extractive matter consisting mainly of sugar or saccharine matter, had no rotatory action on polarised light when in aqueous solution.

Jamaica rum from	Sp. gr.	Alcohol per cent. by vol.	Extract per cent.	Ash per cent.
1. London Docks .....	0·885	75	0·668	0·023
2. Glasgow Docks .....	0·875	75	4·800	0·089
3. Bremen .....	0·875	90	0·568	0·031
4. Obtained direct. ....	0·910	63	2·047	0·098
5. Bremen .....	—	75	0·031	0·025
6. Bremen .....	0·870	63	—	—
7. Brunswick .....	0·875	75	—	—
8. Brunswick .....	0·875	75	—	—
9. So-called artificial. ...	—	48	0·469	0·033
10. So-called artificial. ...	—	72	0·926	0·021

With the exception of No. 5, which was colourless, the above were all more or less darkly coloured.

According to Carles, white of egg will remove from genuine rum

the colouring matter taken up from the cask, but has no action on burnt sugar. The author on shaking up each of the above, as well as solutions of burnt sugar and tincture of catechu, with a sixth of their volume of white of egg, found that they were not decolorised in any case.

Ferrous sulphate, according to Carles, leaves artificially coloured products unacted on, but turns genuine rum dark green. The author found Nos. 1, 2, and 3 were turned distinctly dark green by this reagent; Nos. 4 and 5 indistinctly dark green; Nos. 9 and 10 being unchanged. He therefore concludes that 4 and 5 were naturally coloured, and that 9 and 10 contain burnt sugar, and he considers that this test merely shows the presence or absence of burnt sugar.

F. L. T.

**Examination of Beer for Foreign Bitter Principles.** By DRAGENDORFF (*Chem. Centr.*, 1881, 285—288 and 299—303).—The following method is based on experiments made by the author in conjunction with Kubicki, Jundzill, and Meyke. About 2 litres of the beer to be examined are evaporated on a water-bath until the greater part of the carbonic anhydride and about one-half of the water has been volatilised. The hot liquid is treated with basic lead acetate until no further precipitate is produced. The liquid is filtered as rapidly as possible, and the excess of lead in the filtrate removed with sulphuric acid. The filtrate is neutralised with ammonia to a faint acid reaction, evaporated to 250 to 300 c.c., mixed with four parts by volume of absolute alcohol and allowed to stand for 24 hours. The alcohol is then driven off by distillation, and a portion of the residue shaken up successively with light petroleum, benzene, and chloroform, and another portion is treated in a similar manner, having previously been rendered neutral with ammonia. Pure beer prepared from malt and hops exhibits the following reactions:—Light petroleum absorbs only a small quantity of solids and liquids contained in the beer. The solids have no bitter taste, and give a yellow colour with sulphuric acid. Benzene and chloroform give the same reactions. Similar results are obtained by treating the ammoniacal solution with these solvents. Beer wort behaves like fermented beer.

According to the above method, the following hop surrogates added to beer can be detected:—

1. *Wormwood*.—With light petroleum, the acid solution gives an oil of peculiar odour containing a portion of the bitter principle. By evaporating the extract and treating the residue with sulphuric acid, a brown solution is obtained, which gives the reactions characteristic of absinthin. Similar results are obtained with benzene and chloroform.

2. *Ledum palustre* gives an ethereal oil having the penetrating odour of the plant. Benzene and chloroform extract bitter principles.

3. *Menyanthes trifoliata* (buckbean).—Petroleum extracts but traces of the bitter principle; benzene, however, and especially chloroform, take up larger quantities. The bitter principle (menyanthin) is recognised by its taste and the characteristic odour it produces when treated with dilute sulphuric acid.

4. *Quassia*, like the preceding, is absorbed from its solutions by benzene and chloroform, petroleum extracting only traces.

5. *Colchicum*.—Light petroleum remains inactive, benzene absorbs small quantities of colchicin and colchiceïn.

6. *Cocculus indicus*.—Petroleum and benzene are inactive. Chloroform, or better, amyl alcohol, extract the bitter principle picrotoxin.

7. *Colocynthin*.—Chloroform extracts large quantities.

8. *Willow-bark*.—Salicin is taken up freely by amyl alcohol.

9. *Strychnine* can be extracted only from ammoniacal solutions, benzene and chloroform being the best solvents.

10. *Atropine* and

11. *Hyoscyamine* are extracted from ammoniacal solutions by benzene and chloroform. Certain bitter principles of *Capsicum annuum*, *Daphne Mezereum*, *Onicus benedictus* and *Erythraea Centaureum* are extracted by benzene and chloroform from acid solutions.

12. *Aloes*.—In order to extract this, the above method requires modification. The beer is treated with acetate of lead and shaken up with amyl alcohol. The residue on evaporation gives the characteristic taste and properties of aloes.

13. *Gentian*.—This also requires a modification of the method. After precipitating with normal lead acetate, as in the above, the mixture is filtered and the filtrate treated with sulphuric acid to separate the excess of lead. The solution is evaporated, and the residue acidified with nitric acid and subjected to dialysis. The neutralised solution is again treated with normal acetate of lead, filtered, and the filtrate treated with basic lead acetate and ammonia. This precipitates gentian, which can be isolated from its solution in sulphuric acid by benzene or chloroform.

14. *Picric acid* is not wholly precipitated by basic lead acetate, and cannot be extracted with safety by the above-named solvents. Brunner proposes to digest wool for 24 hours in the beer previously acidified with hydrochloric acid. The wool is subsequently washed, and the picric acid extracted with ammonia. D. B.

**New Test for Glycerol.** By C. BARBSCHÉ (*Chem. Centr.*, 1881, 208).—The characteristic blue coloration which phenol gives with a solution of ferric chloride, was found to be destroyed by glycerol, so that this reaction can be utilised for determining the quantity of glycerol in wine, beer, or other liquids. If dark coloured, or dilute liquids are examined, it is necessary to evaporate to dryness on a water-bath. The residue is extracted with ether and alcohol, evaporated, taken up with water, and tested. Alkaline liquids must be acidified slightly. D. B.

**Reducing Power of Grape-sugar for Fehling's Solution.** By P. DEGENER (*Chem. Centr.*, 1881, 470—471).—From solutions of basic tartrate of copper and sodium containing for every three atoms of copper less than four molecules of free alkali, and from 16 to 18 molecules of Rochelle salt, grape-sugar after 30 minutes' boiling precipitates varying quantities of cuprous oxide, which is always contaminated with organic substances: when the amount of alkali is

raised to 4 mols. per three atoms copper, tolerably exact results are obtained, which may be made quite accurate by employing 6 mols. alkali. The cuprous oxide is then thrown down more rapidly, and is free from organic matter: further addition of alkali does not appear to affect the result up to a certain point. The author is at present engaged in determining the influence of the concentration, excess of alkali, amount of Rochelle salt present, and duration of the boiling. It can, however, be affirmed that by using the above solution with more than 4 mols. free alkali to three atoms of copper, 1 mol. of grape-sugar will always reduce 6 mols. of copper, and not as in the case of Fehling's numbers, from 5.25 to 5.67.

J. K. C.

**Correction of Saccharimetric Test by Inversion.** By P. CASAMAJOR (*Chem. News*, **44**, 219).—The following is a table of factors to be used instead of Clerget's in correcting the direct test of the optical saccharimeter by taking into account the inversion. The factors are arrived at as follows:—

The deviation caused by inverted sugar varies with the temperature; for a solution of sugar, giving 100 to the right, the indication after inversion is 44 to the left, or  $-44$  at  $0^\circ$ ; this deviation becomes  $\frac{1}{2}$  a division less for every degree C. above  $0^\circ$ . Hence if this temperature  $= t$ , then the law of deviation may be formulated:—

$$-\left(44 - \frac{t}{2}\right).$$

If  $D$  = the indication of the saccharimeter before inversion,  
and  $D'$  = " " " " after " "  
then  $D + D'$  = algebraic difference, and for a solution of pure sugar  
 $D = 100$ .

$$\text{Therefore } D + D' = 144 - \frac{t}{2}.$$

If the direct test does not  $= 100$  but  $\Delta$  then—

$$\frac{\Delta}{D + D'} = \frac{100}{144 - \frac{t}{2}}.$$

$$\text{and } \Delta = D + D' \times \frac{100}{144 - \frac{t}{2}}.$$

By calculating  $\frac{100}{144 - \frac{t}{2}}$  for every degree C. we get the factors re-

quired. These are given in the table —

Degrees C.	$\frac{100}{144 - \frac{t}{2}}$	Degrees C.	$\frac{100}{144 - \frac{t}{2}}$
10	0·719	26	0·763
11	0·722	27	0·766
12	0·724	28	0·768
13	0·727	29	0·771
14	0·730	30	0·774
15	0·732	31	0·777
16	0·735	32	0·780
17	0·738	33	0·784
18	0·740	34	0·787
19	0·743	35	0·790
20	0·746	36	0·793
21	0·749	37	0·796
22	0·752	38	0·800
23	0·754	39	0·803
24	0·757	40	0·806
25	0·760		

L. T. O'S.

**Estimation of Phenol in Surgical Dressings.** By K. SEUBERT (*Arch. Pharm.* [3], 18, 321—336).—The author's method is based on the usual one of acting on the phenol with a known amount of bromine-water of known strength, and estimating the excess of bromine by potassium iodide and sodium thiosulphate. Instead of using bromine-water, however, he employs standard solutions of potassium bromate and bromide, and acidifies with sulphuric acid just before using; he then runs the phenol solution into this mixture until a drop of it, after filtration, no longer gives any blue coloration with paper prepared with potassium iodide and starch. It is necessary to filter, because the freshly precipitated tribromophenol has the power of liberating iodine from potassium iodide. The filtration is readily performed by placing a piece of filtering paper over the potassium iodide and starch-paper, a drop of the solution placed on this allowing the liquid to pass but keeping back the solid tribromophenol. In estimating the phenol in a dressing, the author takes 10 grams of the well sampled substance in fairly small pieces, places them in a litre flask, pours on about half a litre of hot water, and then shakes vigorously until all the resinous matter is thoroughly separated from the fibres, after a time adding cold water, cooling, and making up to a litre; a filtered portion of this infusion is employed for the estimation. In the case of cotton wool containing phenol, this filtration is unnecessary.

F. L. T.

**Estimation of Phenol in Urine.** By A. CLOËTTA and E. SCHAEER (*Arch. Pharm.* [3], 18, 241—271).—The authors review the work of E. Baumann on the presence of phenol in urine, and confirm it.

Phenol occurs in urine as a sulphur-compound, by some considered as a salt of phenolsulphonic acid, but by E. Baumann and the authors regarded as potassium phenylsulphate. The phenol cannot be separated from the urine by distillation alone, but will distil off after



adding sulphuric acid (0.3 to 5 per cent.). Phenol occurs as a normal constituent of human urine, and also in larger quantities in the urine of the Herbivora, but the urine of the Carnivora contains it in much smaller quantities or only traces. Under certain ill-defined pathological conditions, especially where the excretion of phenol in the fæces is prevented, the amount in the urine may increase to a hundred times the normal quantity. Where phenol in any form is administered to a patient internally, the whole amount may appear in the urine, sometimes causing it to assume a greenish-brown colour, especially in cases of poisoning; this colour is, however, not proportional to the phenol present; it may occur after operating, but not by application to the uncut skin. An absorption of phenol takes place when applied to the uncut skin, as well as in cases of operations, a precipitate of coagulated albumin separating in the latter cases in larger or smaller quantity on distilling.

The authors found that adding varying quantities of sulphuric acid before distillation had no appreciable effect on the product in the case of "medicated" urines; but in the absence of all administration of phenol; they find a considerable difference in the amount of phenol distilled according as the amount of acid employed is varied.

The actual methods employed in the estimation of the phenol in the distillate were by treatment with bromine-water and weighing the tribromophenol produced; or by comparison of the emulsion formed by its precipitation with a similar emulsion formed from known amounts of phenol; or by the application of the mercurous nitrate test, the colour although not intense being stable. These reactions are applicable only to dilutions exceeding 1 in 10,000, but within this limit the ammonia-bromine test may be employed. The ferric chloride reaction is still less delicate.

F. L. T.

**Aldehyde and Iodoform Reactions.** By B. TOLLENS (*Ber.*, **14**, 1950—1951).—Acetaldehyde, chloral, and other aldehydes of the acetic series reduce alkaline solutions of copper. The aldehydes of the aromatic series have not this power. The characteristic reaction of the aldehydes with ammoniacal silver solutions is rendered much more delicate by the presence of a minute quantity of fixed alkali.

Isopropyl alcohol, lactic acid, and lævulic acid yield iodoform when they are brought in contact with a solution of iodine in potassium iodide and with soda.

When sugar is heated with acids, the distillate contains compounds which reduce Fehling's solution, exhibit the iodoform reaction, and restore the colour to a solution of magenta which has been bleached by sulphurous acid.

W. C. W.

**Qualitative Test for Carbon Bisulphide and Carbon Dioxide in Coal-gas.** By T. O'C. SLOANE (*Chem. News*, **44**, 221).—When the coal-gas is passed through 10—20 c.c. alcoholic potash, the potassium carbonate separates out in aqueous solution, which may be seen by pouring the solution into a test-tube. The presence of carbon bisulphide is shown by the formation of xanthic acid, which is tested for by precipitation with copper sulphate.

L. T. O'S.

**A Modification of Pettenkofer's Test for Gallic Acid.** By E. DRECHSEL (*J. pr. Chem.*, **24**, 45—46).—The author recommends the use of phosphoric instead of sulphuric acid, thus avoiding the interfering action of an excess of sugar, which is not so easily attacked by the former as by the latter acid. D. A. L.

**Estimation of Uric Acid.** By E. LUDWIG (*Chem. Centr.*, 1881, 390).—The urine is treated with a mixture of ammoniacal silver solution and magnesia mixture; and the precipitate, which contains all the uric and phosphoric acids, is filtered off, and washed with very dilute ammonia. It is then decomposed by a warm dilute solution of potassium sulphide, forming potassium urate, which passes into solution. The liquid is filtered; the filtrate slightly acidified with hydrochloric acid and evaporated on the water-bath to a small bulk; and the uric acid which separates out on cooling is filtered off, washed with water, and, after drying at 110°, freed from adhering sulphur by treatment with carbon bisulphide, and subsequently with ether.

T. C.

**Quantitative Estimation of Nicotine in Tobacco.** By J. SKALWEIT (*Arch. Pharm.* [3], **19**, 36—41).—Schloesing in 1846 (*Ann. Chim. Phys.*, 1847, **19**, 230) was the first to estimate nicotine quantitatively in tobacco. His method was to liberate the nicotine by ammonia, take it up with ether, free the ether from ammonia by heating, and titrate the residue with normal sulphuric acid. The author points out the inaccuracies of this method, depending on the difficulty of extracting all the nicotine from the tobacco, and also on the difficulty of ascertaining the neutral point in the extracted dark-coloured resinous mass by means of litmus-paper. His own method is:

The tobacco to be examined is dried at 50° in an air-bath, and pulverised until all passes through a fine sieve. This powder is preserved in an air-tight bottle, the moisture being determined in a small sample at 100°. 20·25 grams of the substance are now weighed out, moistened with 10 c.c. normal sulphuric acid, washed by 200 c.c. of 98 per cent. alcohol into a flask, boiled for two hours with a reversed condenser, allowed to cool, poured into a 250 c.c. graduated flask, and washed up to the mark with absolute alcohol; the mixture is then well shaken up several times. After 6—12 hours, the solution above the tobacco becomes clear; 100 c.c. are then placed in a flask fitted with a two-hole cork, a funnel passing through one hole to the bottom of the flask ending in a fine point, the other hole is connected with a condenser. The chief part of the alcohol is distilled off, and after cooling 30 c.c. of potash solution, sp. gr. 1·159, are added, and the contents distilled until a drop has no reaction on litmus paper. After titrating with decinormal sulphuric acid solution, it is only necessary to divide the number of c.c. by 5, to obtain the percentage of nicotine in the tobacco. F. L. T.

**Separation of Hydrocarbon Oils from Fat Oils.** By A. H. ALLEN (*Chem. News*, **44**, 161—162).—Hydrocarbon oils used for the adulteration of animal and vegetable oils may be divided into four groups. 1st. Oils produced by the distillation of petroleum and bituminous shale, having a density usually ranging between 0·870 and

0.915. 2nd. Oils produced by the distillation of common rosin, having a density 0.965 and upwards. 3rd. Neutral coal oil, being the portion of the products of the distillation of coal-tar boiling about 200° C., and freed from phenols with soda. 4th. Solid paraffin, used for the adulteration of beeswax and spermaceti, and employed in admixture with stearic acid in making candles.

The methods for the detection of hydrocarbon oils in fat oils are based on the density of the sample, the lowered flashing and boiling points, the taste and odour on heating, the fluorescent character of oils of the first two classes, and finally the incomplete saponification of the oil by alkalis. The last process is best performed by heating and shaking with a solution of potash in methylated spirit, evaporating the alcohol after the reaction is complete, dissolving in water, and extracting the unsaponifiable oil by shaking with repeated quantities of ether. The ethereal solution is then evaporated below 100°, and the residue weighed. In most cases this contains nothing more than the hydrocarbon oils; but some oils and waxes after saponification yield larger or smaller quantities of ethereal extract, consisting of alcohols or animal substances such as cholesterin; the larger number, however, of commercial fixed oils do not yield more than  $1\frac{1}{2}$  per cent. of unsaponifiable matter to ether, the chief exception being sperm oil, which gives about 40 per cent. of matter soluble in ether. The method may be relied on to give generally good results, the test experiments being very satisfactory. The hydrocarbon oil having been duly separated can of course be examined by observing its density, taste, and smell, boiling point, &c.

J. K. C.

**Estimation of Fat in Milk by the Lactobutyrometer and Soxhlet's Areometer.** By M. SCHMÖGER and others (*Bied. Centr.*, 1881, 550—552).—Schmöger finds that the extraction of milk residues (dried with sand), by means of Tollens or Soxhlet's apparatus, gives identical results. The lactobutyrometer gives results slightly lower than the analysis. It is to be considered as a very delicate instrument when speed is required, but the writer thinks that the results are too low when calculated by Tollens-Schmidt's table (*Bied. Centr.*, 1879, 229). It is therefore recommended that to the percentage as found by the tables, 0.2 per cent. should be added, or  $x = 0.204y + 1.335$ , where  $y$  = the tenth c.c. ethereal solution of fat, and  $x$  = percentage in weight of the fat. Also alcohol of 92 per cent. is the best to employ, and the individuality of the milk seems to have influence on the results of the butyrometer. The temperature at which readings should be made should be 20°, as at 40° no ether-fat layer separates. The 10 c.c. milk, ether, and alcohol when shaken, should be placed in water at 20°, when the layer separates in half an hour, and the separation is facilitated by the addition of a drop of soda solution. E. Eggert finds likewise that the employment of Soxhlet's apparatus shows a lower quantity than the truth, but considers that Schmöger's correction should be reduced to 0.1 per cent.

E. W. P.

**New Reactions of Milk.** By C. ARNOLD (*Arch. Pharm.* [3], 19, 41—42).—Hitherto, in order to distinguish between fresh and boiled milk,

the odour and taste had to be chiefly relied on. The author finds that a tincture of guaiacum, added to fresh milk, produces at once, or after a few seconds, an intensely blue coloration, which remains for a long time. On cautiously warming the milk to  $40-60^{\circ}$ , the reaction still occurs, likewise at  $70-78^{\circ}$ , but weaker; warmed above  $80^{\circ}$ , the milk remains uncoloured, even on cooling: all milk which has been once boiled behaves in a similar manner. The guaiacum reaction is so delicate that a drop of milk on a watch-glass treated with it, or a drop of milk on a piece of filter-paper touched with a rod moistened with tincture of guaiacum, assumes a blue colour. Sour milk gives the guaiacum reaction, but mineral acids and the alkaline hydroxides prevent it. The author attributes this reaction to the presence of ozone in fresh milk. Emulsions of poppy oil, olive oil, castor oil, and linseed oil are also turned blue by guaiacum.

On treating a mixture of potassium iodide, starch-paste, and milk with old oil of turpentine, a blue zone is produced at the surface of contact, spreading rapidly. Milk boiled for a long time gives the reaction after a few minutes only, after which time the mixture without the milk frequently assumes a blue colour. Milk freed from casein by acetic acid gives no violet coloration characteristic of the peptones with potash and a trace of cupric sulphate, but will do so after the milk has stood for 12—20 hours, a continuous increase of peptone being indicated.

F. L. T.

**Examination of Butter.** By AMBUHL (*Chem. Centr.*, 1881, 475). A satisfactory method of analysis of butter consists of four processes: microscopic examination, whereby an admixture of foreign fat is easily observed by the scarcity of milk fat particles; estimation of fat, which should not be less than 85 per cent.; determination of the sp. gr. at  $100^{\circ}$  C., which should lie between 0.867 and 0.868, and should certainly not be below 0.865; and finally the estimation of volatile acids, according to Reichardt's method.

J. K. C.

**Metaphosphoric Acid as a Test for Albumin.** By C. HINDENLANG (*Chem. Centr.*, 1881, 471).—Metaphosphoric acid exceeds all other known reagents in the completeness of its precipitation of albumin, and can be used with great advantage for this purpose in the case of urine, which contains no other substance to disturb the reaction.

J. K. C.

**Rotatory Power of the Albuminoid Substances in Blood Serum, and their Estimation by this Means.** By S. FREDERICQ (*Compt. rend.*, 93, 465—466).—The numbers given by different observers for the specific rotatory power of the albumin of blood serum show considerable differences, probably due partly to errors of experiment, and partly to the fact that the two albuminoid substances in the serum—true albumin and paraglobulin—have different rotatory powers, and that the albumin is not identical in different species of animals. Paraglobulin precipitated by means of magnesium sulphate from the serum of the blood of the dog, rabbit, bullock, or horse, and purified by repeated solution and reprecipitation, has a rotatory power

of  $-47.8^{\circ}$ . The rotatory power of the albumin from the blood of the bullock, horse, or rabbit, is  $-57.3^{\circ}$ ; from the blood of the dog, its rotatory power is only  $-44^{\circ}$ . The author proposes the following modification of Hoppe-Seyler's process for estimating the albuminoids in the serum. The rotatory power of the serum is determined by means of a Laurent's polarimeter, using tubes 1 or 0.5 dm. in length. The paraglobulin is then precipitated by means of magnesium sulphate from a known volume of the serum, re-dissolved in water, and its rotatory power determined. The number thus obtained subtracted from the first number gives the rotatory power of the albumin. When each of these numbers is divided by the specific rotatory power of the particular substance ( $-47.8^{\circ}$  for paraglobulin, and  $-57.3^{\circ}$  or  $-44^{\circ}$ , as the case may be, for albumin), the quotients give the amount of the substance in 1 gram of the serum. The numbers thus obtained for the total albuminoids agree very closely with those obtained by precipitation with alcohol.

C. H. B.

### Analysis of Photographic Gelatin and Collodion Emulsions.

By J. M. EDER (*Chem. Centr.*, 1881, 397—400, 412—414).—Commercial emulsions are frequently adulterated with a large quantity of glue, and contain but little silver bromide. The following methods are recommended for estimating the value of these preparations.

*Gelatin Emulsions.*—For the estimation of the silver, a weighed quantity of the preparation is diluted with or dissolved in water, and digested with an excess of nitric acid for several hours on a water-bath. The silver bromide collects as a compact precipitate, which may be filtered off, washed, and treated in the ordinary way. It is not safe to determine the silver bromide by mere ignition of the original emulsion, since the gelatin itself leaves a small ash, and it is not unusual for potassium nitrate or bromide to be present. In cases where the silver is present also in the form of iodide or chloride, the silver precipitate is to be treated as in ordinary analysis. Or if great exactness is not required, the silver chloride may be dissolved out by ammonium carbonate and reprecipitated by nitric acid, and the silver bromide separated from the iodide by ammonia. For the estimation of the water, the emulsion is dried at  $100^{\circ}$ , and weighed. Air-dried gelatin emulsion generally loses 8—15 per cent. water at  $100^{\circ}$ . The percentage of gelatin is found by subtracting from the dried residue the silver bromide and potassium bromide as found above.

For the detection of foreign salts, a large quantity of the preparation is pressed between canvas, and 50 grams macerated with cold water for 12 to 15 hours; the soluble salts then diffuse in the water, and may be detected therein by the ordinary methods. Alcohol may be estimated quantitatively by distillation of a portion of the original emulsion, whilst antiseptics, such as phenol and thymol, may be detected by their smell on digesting with sulphuric acid. The presence of salicylic acid may be shown by treating the solution of the emulsion in warm water, with about three times its volume of alcohol, evaporating the filtrate, extracting the residue with ether, evaporating to a small bulk, and applying the ferric chloride test. Excess of silver nitrate is detected by titration with neutral potassium chromate, and

may be determined by dissolving the emulsion in warm water, and titrating with sodium chloride, using potassium chromate as indicator.

*Collodion Emulsions.*—For the estimation of the silver, about 1 gram of the substance is weighed out in a large porcelain crucible, and moistened with strong nitric acid, warmed, and gradually raised to a red heat, the residue being weighed as silver halogen compound. If silver chloride or iodide is present in addition to bromide, the residue after weighing is heated with potassium sodium carbonate, whereby metallic silver and sodium bromide, &c., are formed; on treatment with water, the sodium salts dissolve, and the amounts of iodine, bromine, and chlorine are estimated by the usual methods. The nature and quantity of solvent in the emulsion is determined approximately (as regards ether and alcohol) by fractionating 50–100 grams of the substance. Acetic acid and methyl alcohol are, however, sometimes present in English preparations.

Excess of silver nitrate may be detected by treating a portion with water, and adding hydrochloric acid to the filtrate. For quantitative purposes, the residue insoluble in water should be dried, redissolved in ether and alcohol, and again treated with water and filtered, and the filtrate added to the first filtrate. Excess of soluble bromide or chloride may be detected by a similar treatment.

The detection of preservatives or sensitisers varies in different cases, since the substances used for this purpose are very numerous and varied in character. Some of the more common are tannin, gallic acid, pyrogallol, decoctions of tea and burnt coffee, morphine, cinchonine, quinine, decoction of opium, cane-sugar, grape-sugar, glycerol, albumin, gum, gelatin, resin, and more especially colophonium, shellac, and perhaps guaiacum.

*Collodion-gelatin Emulsions.*—The emulsion is treated with excess of water, whereby the pyroxylin and silver bromide are precipitated. This is filtered off, dried at 100°, weighed, and subsequently carefully ignited after moistening with nitric acid, and the residue of silver bromide weighed; the difference between this and the former weighing gives the pyroxylin. The aqueous filtrate contains the glue, which is estimated by evaporation, &c. The acetic acid is determined by titration of a portion of the emulsion previously treated with water, and the alcohol by distillation after neutralisation of the volatile acids. Ether does not occur in this last form of emulsion. T. C.

**Adulteration of Peru Balsam.** By A. SENIOR (*Analyst*, 6, 204–205).—The sp. gr. of Peru balsam varies from 1.138–1.147, and samples of a lower sp. gr. than 1.138 are to be regarded with suspicion. The consistence of the adulterated sample is usually such as to yield “thick, thread-like, attenuated drops.” The quantitative determination is only of use in such cases when the adulterants tend to increase the weight of benzyl cinnamate, which should amount to about two-fifths or one-half of the total weight of the balsam. To estimate the cinnamic acid, 50 parts of balsam are boiled for two hours with 20 parts of lime and 500 parts of water, water being added from time to time to replace that lost by evaporation. The mixture is then filtered, the residue twice washed with 200 parts of hot

water, and the filtrate acidulated with excess of hydrochloric acid and left to cool, when cinnamic acid crystallises out; this is collected and dried between filter-paper, and finally at  $90^{\circ}$ . The weight of acid ought to be 3 or 4 per cent. of the original sample.

The condition of the residue affords an important indication of the purity, as pointed out by Flückiger (this Journal, Abstr., 1881, 947).

The benzyl cinnamate may be determined by shaking the balsam with carbon bisulphide, in which it is soluble, evaporating the solution (which will be nearly colourless if the balsam be pure), and weighing the residue.

L. T. O'S.

**Testing of Press Yeast.** By E. GEISSLER (*Bied. Centr.*, 1881, 575).—3 or 4 grams of the cake are mixed with water and heated until a thick paste is formed. About 150 c.c. are then heated with a few drops of dilute hydrochloric acid until the liquid no longer strikes a blue with iodine, but an amaranthine red. It is then washed, allowed to settle, collected on a weighed filter, dried, and weighed.

E. W. P.

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## Technical Chemistry.

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**Photographic Platinum Printing** (*Chem. Centr.*, 1881, 175—176).—Ordinary drawing-paper is covered with a layer of starch-paste, and when dry is floated on a solution of ferrous oxalate and potassium platinochloride (100 c.c. water, 3 grams of the platinochloride, 14 grams ferrous oxalate, and sufficient oxalic acid to dissolve the iron salt).—This paper remains unchanged if kept dry, and is three times as sensitive as silvered albuminised paper, and a still stronger picture is obtained by floating on a solution of potassium oxalate. Immediately after exposure, the print is placed in a receiver containing dry calcium chloride, in order to keep it dry until development, which must be carried on under softened white light, or at daybreak or evening. The developer consists of a filtered solution of 100 grams of potassium oxalate in 400 c.c. water, which remains unchanged for a long time. For development the print is floated for some seconds on this solution contained in a porcelain dish heated to 35—80° C.; about 70° gives the best result. The print is then floated on dilute hydrochloric acid (10 c.c. HCl to 800 c.c. water), picture face downwards, and gently agitated for at most 10 minutes, when the acid-bath is renewed, and the process repeated until the new bath remains colourless, showing that all the iron has been removed. The print is finally well washed with water and dried.

T. C.

**Cyanotypes.** By J. M. EDER (*Chem. Centr.*, 1881, 511).—To obtain clear cyanotypes on white ground the following method is recommended:—30 parts of a 5 per cent. aqueous solution of gum arabic are mixed with 8 parts of a solution of 1 part ammonioferric citrate in 2 of water, and to this mixture 5 parts of a solution of



1 part ferric chloride in 2 parts of water are added. The mixture gets thicker on standing, and must be used soon after setting: it is spread over sized paper, which is then dried in the dark. A picture serves as negative. The photograph is developed by a solution of 1 part of potassium ferrocyanide in 5 parts of water; it is then well washed, placed in a 10 per cent. solution of hydrochloric acid, and finally washed and dried.

J. K. C.

**Ink for Photolithography and Phototypography.** By TOOVEY (*Chem. Centr.*, 1881, 288).—10—15 grams of white wax are dissolved in 100 grams of benzene, and treated with 12 grams of lithographic ink. A small quantity of the mixture is then spread over a lithographic stone and rolled with a lithographic roller in very thin layers on glass plates. Finely ground chrome-orange is then sifted over the varnished plates. After drying, a mixture of 3 parts lithographic ink and 7 parts of turpentine is poured on the plates, and when dry a coating of fine "argentan" is sprinkled on the plates. The draughtsman scratches with a point on this layer, having laid the plate on black paper. Through this his work is seen in black lines on a white ground. When the drawing is finished, it can be printed like a negative, the layer of chrome-orange effectually preventing the admission of light.

D. B.

**Water-gas as the Fuel of the Future.** By J. QUAGLIO (*Chem. Centr.*, 1881, 63—64).—The author states that hitherto processes for preparing water-gas by heating carbonaceous matter in retorts, and passing steam through, have not been successful; but he is very hopeful of the processes of Lowe and Strong, who pass air and steam alternately through vertical columns of fuel, the fuel being heated by the air-current, and then decomposing the steam. The gas thus obtained may be rendered luminiferous by means of solid or liquid hydrocarbons.

F. L. T.

**Use of Crystallised Sodium Acetate for Warmers for Railway and other Carriages.** By A. ANGELIN (*Compt. rend.*, 93, 309—311).—Water, on account of its great specific heat, has been used almost exclusively for purposes in which a storage of heat is required. Crystallised sodium acetate,  $C_2H_3O_2Na + 3H_2O$ , contains, however, four times as much useful heat per volume as water; thus, for instance, a warmer of 11 litres capacity, containing 15 kilos. of the salt, would liberate 1,731 cal. on cooling from  $80^\circ$  to  $40^\circ$ , whilst the same warmer filled with water, on cooling between the same limits of temperature, would liberate only 440 cal. Further, the necessary temperature is maintained for nearly ten hours, while, if water is used, the warmers must be changed every two and a half hours. The warmers can be filled once for all, with certain precautions to avoid superfusion; the stoppers must be well soldered; and the whole apparatus perfectly air-tight to avoid loss. As the salt is perfectly stable it can be used indefinitely. Experiments, with a view of introducing this salt, have been made on various railways abroad, and in England on the London and North Western.

V. H. V.

**Boiling and Heating with Gas.** By A. BUHE (*Chem. Centr.*, 1881, 253—256 and 303—304).—The object of the use of non-luminous flames for cooking and heating purposes is to prevent the troublesome formation of soot on the vessels employed, and to utilise satisfactorily the heating power of gas. In order to render gas made from Westphalian coal non-luminous, 100 litres require 220 litres of air, the same proportion holds good for gas made from other sources of German coal and also for ordinary English coal-gas; the highly luminous Boghead gas, however, requires 500 litres of air. For the complete combustion of ordinary gas about 560 litres of air are required for 100 litres of gas, *i.e.*, 40 per cent., to render the gas non-luminous, and 60 per cent. for the subsequent complete combustion of the gas; the latter is taken from the air surrounding the flame. In the remaining portion of the paper, the author discusses very minutely the different kinds of gas-burners, gas-stoves, and ovens employed for domestic purposes. D. B.

**Destruction of the Noxious Gases evolved in the Manufacture of Ammonia from Liquid Sewage.** By L. CHATEAU (*Bull. Soc. Chim.* [2], 36, 194—196).—The ammonia obtained by the distillation of liquid sewage is mixed with hydrogen sulphide, ammonium sulphide, ethyl and methyl sulphides, and traces of other organic compounds. At the works of the Compagnie Urbaine at Arcueil, in order to prevent the escape of these noxious gases into the air, the saturating vessels are made air-tight, and the gases are drawn through the apparatus by means of an aspirator. Between the saturating vessels and the aspirator the gases pass through a purifier containing coke mixed with ferric oxide and calcium sulphate, and kept continually moistened with a solution of ferrous sulphate. After passing through this purifier, the gases are conducted into a furnace of special construction, where they are completely burnt. C. H. B.

**New Method of Extracting Sulphur.** By LA TOUR DU BREUIL (*Compt. rend.*, 93, 456).—The sulphur-ore is heated in a 66 per cent. solution of calcium chloride, at the boiling point of the latter, 120°. At this temperature the sulphur fuses, and runs down to the bottom of the vat in which the heating takes place. Two vats are employed, the calcium chloride solution being drawn off into one, whilst the other is being emptied and refilled, thus allowing the process to go on continuously. The calcium chloride does not act either on the sulphur or on the gangue. The advantages claimed for this method are—(1) The extraction is almost complete, only 2 to 3 per cent. of sulphur remaining in the gangue. (2) The product is very pure, containing only 0.05 to 0.1 per cent. of earthy impurities, and no trace of sulphuric or sulphurous acid. (3) The process can be carried on all the year round, whilst Italian law allows the extraction by *calcaroni* to be carried on only from the end of June to the middle of February. The cost of extraction is about 5 francs per French ton. C. H. B.

**Potassium Chloride in "Osmose Water."** By R. STEINREICH (*Bied. Centr.*, 1881, 573).—Potassium chloride was found in quantity  
i 2

amongst the salts which crystallise from "osmose water;" it causes the formation of molasses, and is removed by dialysis. E. W. P.

**Tripolite compared with Gypsum.** By B. V. LANGENBECK (*Bied. Centr.*, 1881, 430).—Tripolite, a mineral consisting of lime, silica, and ferrous oxide, can be used after heating as plaster of Paris; it is 14 per cent. lighter than real plaster, does not so readily absorb moisture from the air or lose its binding properties, and is cheaper than gypsum. J. K. C.

**Asbestos Fabrics.** By KNOPS (*Chem. Centr.*, 1881, 335).—The author mentions that asbestos imported from Canada is the best and purest in quality. It is brought into commerce as "Bostonite" or "Canadian fibre," in pieces resembling hard stones with adhering fibres. It consists of fine fibres placed side by side in a parallel position, very closely and firmly to one another. The fibres can be easily separated from each other, and when purified, yield a product which can be felted into sheets and woven into cloth. Next to bostonite, the Italian asbestos is the purest. The latter, however, has a higher specific gravity, as it contains a larger percentage of alumina. The fabrics made of bostonite are light, soft, and white, and the sheets are flexible and unctuous to the touch. D. B.

**Malleable Cast Iron and the Cementation of Steel.** By FORQUIGNON (*Ann. Chim. Phys.* [5], 23, 433—554).—Malleable cast iron is the product of a special metallurgical operation. It is produced by submitting casts to a process of cementation in "cements" of different kinds; such as ferric oxide, chalk, &c. The metal, which before the treatment was hard, fragile, and easily fusible, becomes soft, malleable, easy to work with tools, and difficult to melt. The author states that castings which are very grey or contain much manganese give bad results. Spotted or white iron obtained from very pure ore yields the best results. The softening process is applicable only to small objects, such as keys, spurs, buckles, &c. The operation is not conducted with success when the diameter of the articles exceeds 0.03 meter to 0.035 meter. The duration of the experiment varies with the diameter of the object and the quality of iron which it is desired to obtain, from 24 hours to 6 days, and upwards. The temperature of the furnace is generally bright cherry-red (about 1,000°), and the "cement" usually employed is ferric oxide, which is broken into grains, and the objects to be cemented are imbedded in it, in large pots. These are afterwards hermetically sealed and placed on the floor of the furnace. Care must be taken to allow them to cool before opening.

The following are the results obtained by employing various "cements":—

1. *Wood Charcoal*.—The cast is considerably softened. From 50 to 55 per cent. of the combined carbon is changed into graphite, although the body retains its solid state. There is a considerable diminution of silicon. It is obvious that the theory which attributes softening to a purely oxidising action is incorrect.

2. *Iron Filings*.—A considerable quantity of carbon and silicon is absorbed by the iron filings. At the same time graphite is deposited. The "cement" in this case has exercised a decarbonising action.

3. *Siliceous Sand*.—There is in this case a gain in silicon and a loss in carbon. The carbon appears to reduce the silica in presence of iron.

4. *Quick-lime*.—Lime exercises a most violent action on the iron. It eats into the surface and covers it in places with a blackish semi-fused crust. The total carbon undergoes a remarkable diminution. The silicon is reduced by 35 per cent. after 24 hours' cementation.

5. *Bone Dust*.—The total carbon is very little diminished, and there is scarcely any graphite formed. The author states that this is probably due to the bone ash being a bad conductor.

6. *Colcothar*.—The surface of the metal is attacked, and there is a gain in silicon, but there is less combined carbon and much more graphite than in samples heated for the same length of time with hæmatite.

7. *Colcothar and Salt*.—The introduction of salt does not prevent the removal of silicon nor the increase of graphite; but it checks the action of colcothar on the surface, and on the whole the mixture yields excellent results.

In addition to analysing the specimens before and after cementation, the author has determined some of the physical properties of the casts; such as the breaking strain, the elongation before breaking, and the limit of elasticity. The specimens used in the experiments were cast in the form of bars. The section was accurately determined by means of a spherometer, and then two marks, distant 0.1 meter from each other, were made on the surface. The bar was then attached to a vertical machine, and the marks read off with a cathetometer. The weight, which could be varied from 1 kilo. to 100 tons, was then applied. After each increment of weight, a reading was taken with the cathetometer until the point of rupture was reached. By this means the elongation of the bar and the point of rupture were obtained. Taking the successive charges referred to the unit of section as abscissæ, and the observed elongations as ordinates, a curve was constructed whose form showed the position of the limit of elasticity. The author states that: 1. *The resistance to rupture* is always more than doubled, sometimes more than quadrupled, by cementation. It increases with the duration of the heating. 2. *The elongation* varies with the resistance to rupture; but, after passing a point which it reaches in from 72 to 144 hours, it has a tendency to diminish somewhat. 3. *The limit of elasticity* is lowered by each cementation. 4. It appears that each variety of cast has a particular kind of cement which suits it and produces a better effect than all others.

Malleable casts occupy an intermediate position between grey cast iron and steel. They differ from the former in the peculiar nature of their amorphous graphite as well as by their great tenacity. They are distinguished from steel by their slight elongation and tenacious retention of graphite. The author states that this graphite is a peculiar form of carbon, differing in its structure, mode of formation, and derivatives, from the crystalline variety which is ordinarily met with in iron. It is amorphous, and is formed by the action of heat on a solid bar at about 1,000°.

*Cementation in Gaseous Media.*—Hydrogen exerts a decarbonising action on iron at about  $800^{\circ}$ , giving rise to gaseous hydrocarbons, and a certain quantity of hydrogen remains combined with the carbon unremoved. The author states that it is probably methane which is formed. Cyanogen is formed when iron is heated in a current of nitrogen.

The author draws the following conclusions from his experiments :—

1. A malleable casting always contains amorphous graphite.
2. A casting may lose carbon and still remain fragile if the remaining carbon is not in the form of graphite, or if the initial quantity of graphite is not increased.
3. A casting may become malleable without losing a sensible part of its total carbon.
4. A manganiferous casting, to which silicon is added, is improved by cementation.
5. Hydrogen and nitrogen deprive the casting of some of its carbon. This is the case only when it can become malleable without formation of graphite.

J. I. W.

**Dephosphorising Iron in the Bessemer Process.** (*Chem. Centr.*, 1881, 431.)—The invention which forms the subject of the present paper refers to a process of removing phosphorus from phosphoriferous pig iron in the production of "flowing iron" in the Bessemer converter. To carry out this invention the basic bricks, patented by Thomas, are employed, and immediately before the introduction of the metal into the converter, a quantity of lime, or a mixture of lime and ferric oxide, is thrown into the converter. This is prepared by mixing 4—6 parts of magnesium limestone free from silicon, with 1 part of ferric oxide, and calcining the mixture after forming it into bricks. Twice the weight of this is used compared with the amount of silicon and phosphorus contained in the charge. The mixture is exposed to a strong blast for 6—10 minutes, the slag in the converter is then removed, and a smaller quantity of mixture introduced. The whole is again heated strongly, the time of completion depending on the quantity of phosphorus present in the charge. An indication of the end of the operation is the appearance of brown fumes; it is, however, best to take a sample of the metal from the converter, and hammer it. If the metal is hard, the heating must be continued.

D. B.

**Ferro-silicon.** By BIERMANN (*Chem. Centr.*, 1881, 430).—It has been clearly proved that castings are now made which are perfectly free from blisters, by the addition of a highly siliceous iron immediately before the formation of carbonic oxide, the presence of which is known to be the cause of the blistering of iron. The product, however, is said to be very inferior in quality, owing to the presence of silicon in the metal. When manganese is used, the ferric oxide is reduced and the evolution of gas prevented; the product is a silicate of iron and manganese, and is more fusible than silicate of iron: hence it is preferable to use manganese in conjunction with silicon,

the casting obtained being perfectly free from silicon, manganese, and blisters. D. B.

**Galvanising of Iron.** By J. B. JONES, H. W. SHEPARD, and R. SEAMANN (*Chem. Centr.*, 1881, 335).—The essential feature of the process consists in destroying the injurious iron salts on the surface of the iron before insertion into the metallic bath, and in preventing oxidation before insertion. Thus the use of hydrochloric acid and the subsequent drying in ovens is abandoned. The sheets are well cleaned and introduced into a liquid consisting of a 1 or 2 per cent. solution of an organic or metallic chloride, the bases of which are in a positive ratio to iron. They are then placed in a solution of equal parts of water and chlorine compounds of organic or metallic bases, the salts of which are fusible at the temperature of the metallic bath. From this solution they are at once brought into the metallic bath, consisting of zinc or an alloy of zinc, and exposed to the action of the bath until the necessary coating has been obtained. The authors use an alloy of zinc, tin, lead, and nickel, which is said to have a greater degree of fluidity, so that an effectual coating is obtained with a smaller quantity of metal. D. B.

**Separation of Copper from the Precious Metals.** By T. STERRY HUNT (*Chem. News*, 44, 198—202).—The principal wet processes hitherto used for extracting copper from its ores are the following:—

1. Those in which the copper in sulphuretted ores is rendered soluble in water by calcining them with a portion of common salt, after a preliminary roasting to remove the greater part of their sulphur: by this means the metal is converted into a chloride, or into the sulphate if sodium sulphate is used.

2. Those methods in which free hydrochloric or sulphuric acid is used to dissolve the copper from oxidised or roasted ores. These, while simple and efficient, are too costly, except in certain localities where hydrochloric acid is a waste product.

3. The method in which a hot solution of ferrous chloride with common salt is used to convert the oxidised copper into a mixture of cupric and cuprous chlorides; the latter, although nearly insoluble in water, is then dissolved by the aid of sodium chloride. The copper is precipitated from this solution by metallic iron.

When this method is applied to the treatment of copper ores containing silver, the latter is converted into a chloride which is soluble in strong solution of sodium chloride, and is then with difficulty separated from the chlorides of copper. Various plans have been suggested for extracting the dissolved silver from such solutions before throwing down the copper by metallic iron. The most efficient method of effecting this is that patented by Claudet. It depends on the almost complete insolubility of silver iodide in solutions of sodium chloride, and consists in adding to the solution, in which the proportion of dissolved silver has previously been determined, a dilute solution of a soluble iodide just sufficient in amount to convert the whole of the silver into the iodide. The precipitate which separates after forty-

eight hours' standing is washed with dilute hydrochloric acid to remove adherent copper salts, and then consists chiefly of a mixture of lead sulphate with silver iodide, which is reduced by metallic zinc, the iodine being thus recovered for further use.

The extraction of copper from its ores by roasting with salt is limited to pyrites poor in copper, which yield by their previous calcination a large proportion of ferric oxide, the presence of this being necessary to the effectual chloridising of the copper in the furnace. When applied to richer ores, this method fails to render the whole of the copper soluble.

The author has devoted much time to the metallurgical problem thus presented, and in conjunction with J. Douglas has devised a novel wet process for the extraction of copper from its ores, based on the reactions described by Wöhler between sulphurous acid and a solution of cupric chloride, which gives rise to insoluble cuprous chloride, with elimination of one half the chlorine as hydrochloric acid, and simultaneous formation of sulphuric acid. The resulting acid solution, when brought in contact with cupric oxide, will take up as much copper as it originally held, which may, in its turn, be thrown down by sulphurous acid. In this way the solution of copper from an oxidised ore and its precipitation as cuprous chloride, may be repeated indefinitely, provided chlorine be supplied each time by the addition of a sufficient amount of some soluble chloride. The process is described in detail in the original paper.

It is mentioned that, unlike the method of chlorination by roasting with salt, that depending on the use of a solution of ferrous chloride with salt is a general one, applicable to all naturally or artificially oxidised copper ores, which may be readily and cheaply chlorinated by its aid. When applied to copper ores containing silver, however, this shares with the salt-roasting process the disadvantage that the silver is at the same time chloridised and dissolved, while the cupric chloride formed by the reaction between the oxide of copper and the ferrous chloride precludes the use of Claudet's method of precipitating the dissolved silver by a soluble iodide.

D. B.

**Amalgamation of Gold Dispersed in Sulphides.** (*Chem. Centr.*, 1881, 206.)—The ores are in the first place reduced to a powder in crushing mills or other machines. The product should pass through a sieve, with 3600 meshes per square inch. It is then transferred to cylinders made of fire-clay set in furnaces, each containing four cylinders. The ore is brought into the uppermost cylinder, which is the lowest in temperature; it then gradually passes to the second, third, and fourth cylinders. The passage is effected by means of mechanical agitators, and should occupy four hours. The ore is then cooled and treated with hot vapours of mercury in automatic amalgamators. After cooling, the mass is agitated strongly in water. The amalgam of mercury and gold is rapidly separated by this treatment.

D. B.

**Ethereal Oils.** By E. GEISLER (*Chem. Centr.*, 1881, 505).—Haensel's patent oils are extracts of essence of lemon and orange concentrated by distillation. Their aroma is exceedingly strong, and

their sp. gr. is greater than that of the ordinary essences, oil of lemons having a sp. gr. of 0·9003, and oil of oranges 0·909. They are both acted on by sodium, and turn the plane of polarisation to the right.

J. K. C.

**Acorns and Earth Puffs as Distillery Materials.** By H. DILL (*Bied. Centr.*, 1881, 557).—Shelled acorns having the composition: starch, 20·28; gluten, 18·00; tannic acid, 2·86; fibre, 7·15; extractive matter, &c., 51·71 per cent. yield, when mashed with wheat and rye, a fine spirit. The tubers of *Helianthus tuberosus*, being rich in inulin and sugar, have for long past been employed in Belgium and Hungary as a source of spirit. The analysis of these tubers is as follows:—Sugar, 14·8; inulin, 3·0; mucilage, 1·22; albumin, 0·99; salts, 1·72; fibre, 1·22; water, 77·05, per cent.

Some technical directions for fermentation are also given.

E. W. P.

**Analysis of White Wine from Erfurt.** By W. HADELICH (*Chem. Centr.*, 1881, 394).

Specific gravity .....	0·9976
Alcohol.....	6·55
Extract.....	2·28
Total acids, calculated as tartaric acid.....	0·62
Free tartaric acid .....	absent
Combined tartaric acid .....	0·23
Malic acid and tannin .....	{ comparatively large
Glycerol .....	
Ash, with alkaline reaction .....	0·281
Potash .....	0·1294
Lime.....	0·0042
Magnesia .....	0·025
Phosphoric acid .....	0·0527
Sulphuric acid.....	0·0421
Chlorine .....	0·0054

*Composition of Ash.*

K <sub>2</sub> O.	Na <sub>2</sub> O.	CaO.	MgO.	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CO <sub>2</sub> .
46·08	3·83	1·51	8·93	0·33	trace	2·18
	SiO <sub>2</sub> .	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	Cl.		
	1·56	18·79	15·00	1·95		T. C.

**Alkaline Earths in Wine.** By R. KAYSER (*Chem. Centr.*, 1881, 394).—The ashes of wine always contain calcium and magnesium salts. The amount (3 to 11·4 mgrms. in 100 c.c. of wine) of calcium is greatest in young wines, and gradually diminishes with age, probably in consequence of the separation of neutral calcium tartrate. The amount of magnesium on the other hand remains almost constant, and is always in excess of the calcium. The largest amount of magnesium found by the author was 24 mgrms. in 100 c.c. of Malaga wine. The



phosphoric acid and magnesia show a constant proportion of 10 : 6, corresponding with the formula  $\text{MgHPO}_4$ . T. C.

**Bouquet of Rhine Wine.** By A. v. BABO (*Bied. Centr.*, 1881, 574).—The famed bouquet of the wine from Riesling grapes is produced by the action of frost, wines from other grapes also possess a like bouquet if the grapes are frozen. E. W. P.

**Action of Light on Beer.** By G. BECKH (*Bied. Centr.*, 1881, 574).—The changes which are frequently noticed as occurring in beer, are due to the action of sunlight affecting the ferment in the beer, and producing lactic acid ferment and *Saccharomyces exiguus*. E. W. P.

**Improvement in Sugar Manufacture.** By N. MEHRLE (*Bied. Centr.*, 1881, 573).—The sections of the sugar beets are treated with a dilute solution of ferrous or ferric sulphate, which fixes the nitrogenous matter in the cells. The percentage of sugar in the dry matter is consequently raised, and the final operations greatly facilitated. E. W. P.

**Preparation of Sugar without Molasses.** By DUBRUNFAUT (*Bied. Centr.*, 1881, 553).—The syrup obtained in the manufacture of beet-sugar is subjected to the process of "Lime Osmose" in which sufficient lime is added to form calcium saccharate, whereby potash and soda are liberated. This mixture is then placed on a dialyser, the alkalis passing into the "osmose water" through the septum, a purer syrup still containing lime salts is obtained; a little more lime is then added, carbonic anhydride passed in, and the resulting purified syrup, after addition of a fresh supply of beet juice, is evaporated, allowed to crystallise, and the new syrup again treated as before.

E. W. P.

**Changes which Sugar Undergoes in Crystallising.** By FLOURENS (*Bied. Centr.*, 1881, 572).—Saccharose solutions which contain glucose, are to a certain extent inverted during crystallisation, and this is due to free acids which accompany the glucose; and even if the solutions are rendered alkaline, the change will still take place, colouring matters being produced, and the products becoming dark.

E. W. P.

**Deterioration of Sugar by Keeping.** By H. PELLET and H. BULLIER (*Bied. Centr.*, 1881, 573).—A sample of cane-sugar was analysed in 1876, and again in 1878, and it was found that the crystallisable sugar had decreased by 10 per cent., whilst the glucose had correspondingly increased. E. W. P.

**Absorption of Sugar by Animal Charcoal.** By H. MOTT (*Bied. Centr.*, 1881, 570).—10 grams animal charcoal will absorb 0.30—0.35 per cent. from a solution of pure sugar. From solutions of crude sugar, 0.1—0.66 per cent. of substances which polarise light is absorbed, but the quantity is reduced to 0.35 after inversion. Perfectly

dry charcoal absorbs best. Two grams are sufficient to decolorise a filtered sugar solution which has been properly precipitated by basic lead acetate, and this quantity may be employed without loss, as the amount removed by absorption is very small. E. W. P.

**On Saponification.** (*Dingl. polyt. J.*, **242**, 55.)—Scheurer mentions that, in the present methods of soap-making, part of the alkali and fatty acids remain uncombined, and when the soap is used for dyeing purposes, the free alkali injures the colours very considerably. In order to avoid this, he recommends to effect the saponification under pressure; on investigation, however, this was not found to be successful.

Referring to the preparation of soap in the cold, Köchlin found that when made with olive oil (*huile tournante*) and soda-ley the soap should not be stirred for more than two or three minutes, otherwise it is resolved into its original constituents. With potash-ley, continued agitation is necessary.

Menzies prepares potash soap by dissolving 50 kilos. potash in 50 litres water, and adding 210 kilos. purified tallow, previously melted. The mixture is well agitated and transferred to frames, where it is kept at rest for three or four days under cover: it is then brought into drying rooms and dried for a week. Thus 310 kilos. soap are said to be produced. D. B.

**Preparation of Purified Oleïc Acid.** (*Chem. Centr.*, 1881, 14.)—60 parts of oil soap are dissolved in 4 times as much boiling water, decomposed by 10 parts sulphuric acid and boiled until the separation of the oleïc acid is complete; this is washed with hot water, and 4 parts of lead oxide are then dissolved in the oleïc acid, and to the still hot fluid are added 60 parts of alcohol (0·820) heated to 65°. After 24 hours' digestion, the residue is well pressed and decomposed by 1 part of hydrochloric acid, the oleïc acid repeatedly washed with water and finally filtered. The yield is about 30 parts of purified oleïc acid of bright yellow colour, and with but a faint smell of olive oil; its sp. gr. is 0·897. F. L. T.

**Extraction of Fat from Bones by Light Petroleum.** By C. THIEL (*Chem. Centr.*, 1881, 13).—The bones, either whole or in small pieces, are digested with light petroleum for some hours under a pressure of several atmospheres. The oil is then run off, and distilled by a steam-jet; the fat (about 7·48 per cent. of the bones) is at once ready for the market. The vessels are best made of galvanised iron. F. L. T.

**Flour Rendered Uneatable by Free Fatty Acid.** By C. BERNBECK (*Arch. Pharm.* [3], **18**, 337—340).—A sample of flour submitted to the author for examination was found under the microscope to be an unadulterated "seconds" flour with immaterial traces of mould. Its taste was at first like wheat, then however bitterish, with a prolonged harsh taste in the throat. The odour was mildewy, and undefinably objectionable. On heating, a penetrating fatty odour was

produced; the flour shaken with water reddened a piece of blue litmus-paper which was well stirred up with it; the distilled water, however, with which it was shaken up remained neutral, showing that the acid present was insoluble. By extracting with ether and evaporating, an oily residue was obtained, strongly acid to litmus, with the same objectionable odour as the flour but stronger. The results of the author's examination were:

Water.....	12.9	per cent.
Ash.....	1.1	"
Gluten .....	32.0	"
Fat, with free fatty acid.....	1.65	"
Wheat starch and bran .....	52.35	"
<hr/>		
100.00		

On making bread from a sample of this flour, it tasted and smelt of rancid fat, and was nauseating to eat.

On adding  $\frac{1}{4}$  per cent. of oleic acid to an ordinary dough and baking, bread with a similar taste and odour was produced, thus proving that the unfitness of the flour in question for food was due to the presence of rancid fat.

F. L. T.

**Creaming by the Aid of Heat.** By K. BECKER (*Bied. Centr.*, 1881, 571).—Milk is placed in a closed vessel resembling Swarts', and heated by warm water for two hours at 50°, then it is cooled for 24—60 hours, after which the cream is removed. The cream and skim milk thus produced keep well, and the milk, which contained previously 3.13 per cent. fat, after 24 hours' contains only 0.56 per cent.

E. W. P.

**Experiments with an Improved Form of Reimer's Creamer.** By M. SCHRODT (*Bied. Centr.*, 1881, 571).—A short description of the creamers is given, and the results are satisfactory, as high as 91.53 per cent. of the cream having been removed from the milk.

E. W. P.

**Tesca's Separator.** By LABESIUS (*Bied. Centr.*, 1881, 572).—To obtain the best results, the milk must not pass through too quickly, and it should be warmed. Thus from 5 kilos. milk, skim milk containing 0.5 per cent. fat is obtained in one minute.

E. W. P.

**New American Process for Making Cheese.** By E. CHESNEL (*Bied. Centr.*, 1881, 552).—By this process, butter, milk, and skim milk are employed for cheese-making, and the acid of the butter milk is removed. A warm mixture of the two are allowed to become sour, and then at 30°, 60 grams of "anti-huffing extract" is added. After ten minutes Hansen rennet is added, and the whole heated to 35—36°, when the perfectly sweet curd may be separated, salted, and pressed.

E. W. P.

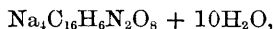
**Preparation of Colouring Matters by the Action of Diazo-anisols on Naphthols and Naphtholsulphonic Acids.** (*Dingl.*

*polyt. J.*, **242**, 61.)—For the preparation of diazo-anisoils, the following amido-compounds are used:—Amidophenylmethyl ether, amido-anisoil or anisidine,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ ; amidophenylethyl ether, or amidophenetol,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$ ; amidophenylamyl ether, or amidophenamylol,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OC}_5\text{H}_{11}$ ; and the corresponding methyl, ethyl, and amyl ethers of amidocresol,  $\text{NH}_2\cdot\text{C}_7\text{H}_6\cdot\text{OH}$ ; and the two isomeric amidonaphthols,  $\alpha\beta\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$ . For the preparation of the diazo-anisoilsulphonic acids, the following amido-compounds are used:—Anisidinesulphonic acid,  $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{SO}_3\text{H})\cdot\text{OMe}$ ; amidophenetolsulphonic acid,  $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{SO}_3\text{H})\cdot\text{OEt}$ ; amidophenamylolsulphonic acid,  $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{SO}_3\text{H})\cdot\text{OC}_5\text{H}_{11}$ , and the methyl, ethyl, and amyl ethers of amidocresolsulphonic acid,  $\text{NH}_2\cdot\text{C}_7\text{H}_5(\text{SO}_3\text{H})\cdot\text{OH}$ , and amidonaphtholsulphonic acid,  $\text{NH}_2\cdot\text{C}_{10}\text{H}_5(\text{SO}_3\text{H})\cdot\text{OH}$ . By the combination of 1 mol. of the diazo-bodies with 1 mol. of the naphthols or naphtholsulphonic acids, red or violet azo-colouring matters are produced.

For the preparation of the scarlet colouring matter called “anisoil red,” 10 kilos. anisidine are dissolved with 30 kilos. concentrated hydrochloric acid, in 200 litres of water, and converted into diazoanisoil hydrochloride by the slow addition of an aqueous solution of 5.61 kilos. sodium nitrite. By introducing the mixture into an alkaline solution of 18.2 kilos. sodium  $\beta$ -naphtholmonosulphonate, the colouring matter is separated as a red precipitate. The phenols and cresols give scarlets; the ethers of the amidonaphthols give violets.

To prepare the colouring matters from diazoanisoilsulphonic acid, 1 kilo. anisidine is heated with 4 kilos. sulphuric acid, of 1.48 sp. gr., for several hours on a water-bath, until the mixture is perfectly soluble in water. The excess of acid is removed with gypsum, and sodium carbonate added to the filtrate, to form sodium anisidinesulphonate. In order to prepare the colouring matter from diazoanisoilsulphonic acid, 16.5 kilos. anisidinesulphonic acid are dissolved in 20 kilos. concentrated hydrochloric acid in 200 litres water, and converted into diazoanisoilsulphonic acid by the addition of 5.61 kilos. sodium nitrite. This is added to an alkaline solution of 11.7 kilos.  $\beta$ -naphthol, or 18.2 kilos.  $\beta$ -naphtholmonosulphonic acid, or 24.7 kilos.  $\beta$ -naphtholdisulphonic acid. The red colouring matter is separated by the addition of sodium chloride. It is filtered and dried.

The nitrosulphonic acids of  $\alpha$ -naphthol, especially dinitronaphtholsulphonic acid, form fine colouring matters, soluble in water. According to Claus, azophthalic acid is prepared by nitrating phthalic anhydride, dissolving the nitrophthalic acid in a dilute soda solution, and adding to 100 grams of acid an amalgam of 60 grams sodium and 4 kilos. mercury. Sodium azophthalate,



separates in fine yellowish-red crystals. By decomposing with hydrochloric acid, azophthalic acid,  $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_8$ , is obtained in the form of yellow crystals.

In the preparation of alizarin, Domeier and Marzell recommend to saturate the aqueous solution of the “soda-melt” with sulphurous acid. The precipitated alizarin is filtered, pressed, and the filtrate treated with calcium, barium, or strontium hydroxide. The caustic

alkali thus produced is utilised for a further melt, and the precipitated sulphates are decomposed with hydrochloric acid, and the sulphurous acid evolved is re-introduced into the melt. Römer proposes to treat an ammoniacal solution of alizarin with zinc-dust, in order to form deoxyalizarin,  $C_{14}H_{10}O_3$ , which crystallises in pale-yellow needles.

D. B.

**Manufacture of Galleïn.** By A. MONTLAUR (*Chem. Centr.*, 1881, 395).—For the preparation of pyrogallol, gallic acid is dibrominated in the cold, and without increase of pressure, in a cast-iron enamelled digester, and as soon as the evolution of the hydrobromic acid has ceased, it is heated with  $1\frac{1}{2}$  equivalent of bromine at  $100^\circ$ . After separation of the excess of hydrobromic acid or of bromine, sodium sulphhydrate is added, and the whole heated in the closed digester at  $60^\circ$ , after which the mass is treated with alcohol, decanted, and the alcohol distilled off in a copper. 60—70 per cent. of pyrogallol is obtained in this way, with a loss of 5—10 per cent. bromine. The pyrogallol may be converted into galleïn by treatment in the retort with half its weight of phthalic acid in the ordinary way. Galleïn is obtained in the form of paste by the addition of  $\frac{1}{15}$  of the requisite quantity of soda, and filtering after an hour's time. The sodium is now present entirely as metagallate. The mass is then treated with the rest of the soda at a boiling heat. This process is repeated several times, when the galleïn will be so far purified that it does not oxidise on exposure to the air.

T. C.

**Dye-stuff from Cöruleïn.** By PRUD'HOMME (*Chem. Centr.*, 1881, 395).—The cöruleïn is fused with an aniline salt, until a portion taken out dissolves in dilute soda, with a brownish-yellow coloration, without a trace of green. Hydrochloric acid is evolved in considerable quantity during the reaction. The fused mass is poured into water, thrown on a filter, and washed with boiling water, until the filtrate comes through colourless. The new dye-stuff may then be extracted from the residue by alcohol, in which it dissolves, forming a yellow liquid, with a beautiful green fluorescence. On pouring this solution gradually into water and exposing it to air, the dye-stuff separates out in brown flocks; those give a green liquid with sodium sulphite, becoming blue on addition of ammonia. Dyeing operations with this substance only take place slowly, and require a boiling heat. With iron mordant, it gives a bluish-green; with iron and alumina, a lighter green; with alumina (for reds), an indigo-blue; with alumina (for rose), a violet-blue; with weak iron mordants, a bluish-green; and with chrome mordants, a green; whilst cöruleïn gives with the same mordants yellowish-greens. The new dye-stuff is probably derived from cöruleïn by the substitution of several hydroxyl-groups by NHPH-groups.

T. C.

**Resists for Aniline-black.** (*Chem. News*, 44, 76.)—Gum-water containing 50 grams per litre of ammonium or potassium thiocyanate completely resists aniline-black. By the use of these salts, reds, greens, blues, violets, and catechu colours are obtained pure and well defined

on a black ground. The aniline colours whether applied with tannin, albumin, or arsenic, are mixed with 50—60 grams per litre of either of the thiocyanates. With acid colours, lead thiocyanate should be used. For alizarin-reds, ammonium thiocyanate may be used instead of red liquor. In photography, the thiocyanates may with advantage be substituted for sodium thiosulphate, since they are not so liable to cause spots, and are more easily washed away. C. H. B.

**Dyeing with Methylene Blue.** (*Dingl. polyt. J.*, 242, 64).—This colouring matter is produced by converting dimethylaniline hydrochloride into nitrosodimethylaniline by means of sodium nitrite. By treatment with sulphuretted hydrogen the product is converted into amidodimethylaniline, which is oxidised with ferric chloride.

The tannates of aluminium, iron, chromium, uranium, nickel, barium, and copper, give bright and fast colours when dyed with methylene blue. In dyeing it was found that the best results were obtained when distilled water was used; and in order to obtain a similar effect with river water, a mixture of 2 grams soda, and 2 grams normal sodium phosphate was added to every litre of the water.

When Turkey-red oil is added to the dye-bath, negative results are obtained; hence the material must be oiled before dyeing. It is then treated twice with ferrous acetate of 1° Bé, hung up to dry in the cold for two days, and fixed in a bath of soda water-glass (5 grams per litre), in order to be dyed in tannin. For 1 kilo. cotton 300 grams tannin are used. After washing, the material is dyed in the following bath:—100 litres of river water, 200 grams soda, 200 sodium phosphate, and 38 methylene blue. A very dark blue is obtained, which has a copper lustre, and can be soaped without losing its fastness. In order to obtain lighter blues, the oiled material is soaked in a solution of alum (20 grams per litre). It is hung up to dry in the cold for two days, and fixed in a bath consisting of 100 litres water of 50°, 500 grams chalk, and 100 of crystallised sodium arsenate. After washing the cotton is dyed as above.

Methylene blue resists the action of soap, chlorine, and light, but does not stand caustic alkalis as well as indigo. D. B.

**New Method of Painting on Glass.** By J. B. MILLER (*Dingl. polyt. J.* 242, 57—60).—Hitherto the difficulty in glass painting has been the want of uniformity and evenness in the colours produced. This the author appears to have surmounted by a new method, which consists in laying on the colour in the form of a fine spray, and not with a brush. In order to effect this and the subsequent treatment of the glass, a special apparatus has been devised, which is described very minutely in the original paper. D. B.

**Silvering of Glass.** By H. E. BENRATH (*Chem. Centr.*, 1881, 446).—The method resembles Martin's process of silvering glass, the difference being that the liquid employed is poured on the glass. The following solutions are required:—800 grams of silver nitrate and 1,200 grams ammonium nitrate dissolved in 10 litres of water, 1,300 pure fused soda dissolved in 10 litres of water, 150 grams loaf-sugar,

and 15 grams tartaric acid dissolved in about 0.5 litre of water, the solution being kept at rest for half an hour, after which it is diluted to 4,200 c.c.

D. B.

**Bleaching.** By J. M. CLEMENT (*Chem. Centr.*, 1881, 77).—According to a French patent, the stuffs are first placed in water containing yeast to remove the weaver's glue, which it does in twelve hours. They are then transferred to an oxidising bath consisting of 1,000 litres of water and 500 grams of a new oxidising mixture (potassium permanganate 670 grams, and potassium dichromate 330 grams). After an hour, the material is transferred to a second bath consisting of 1,000 litres of water, 1,500 grams of sodium sulphite or hyposulphite, 750 grams of sulphuric or 875 grams of hydrochloric acid, and 250 grams of sodium or potassium carbonate. After two hours' stirring, the materials are rinsed and transferred to a bath of 370 grams of sodium or potassium hypochlorite, and 2,500 grams of sodium carbonate in 1,000 litres of water. The bleaching of cotton wool is generally complete in 8–10 hours; it has only to be rinsed, placed in a second bath for an hour, again rinsed, and finished in the usual manner. With linen these operations are to be repeated in the same order—three operations generally sufficing. In the case of wool, instead of treatment with yeast, the sweat is removed by means of a known bath or by purified urine. The raw wool is first melted with oleic acid or *huile tournante*, and is, after 1–2 hours, washed with warm or cold water until the latter runs off colourless. It is then placed in a bath of 1,000 litres of water and 15 litres of a liquid (66 parts [by vol.] of aqueous ammonia and 33 parts, by vol., of benzene or other hydrocarbon). The mixture is well stirred, the wool dipped in, and washed as usual. The removal of the fat and the bleaching is complete in a few minutes. The decolorisation of sponges takes place best in baths of oxidising matter and a vegetable acid, preferably oxalic.

F. L. T.

**Copying Ink for Transcribing Letters without a Press.** By J. ATTFIELD (*Chem. News*, 44, 141).—Ten volumes of ink are reduced by evaporation to 6 vols., and 4 vols. of glycerol are then added; or some ink is made of double the usual strength and diluted with about its own volume of glycerol. The letter, &c., written with this ink is simply placed in an ordinary thin paper copying book, and a leaf of the latter is pressed down upon it with the hand, just as if using a sheet of blotting-paper. Any excess of ink is removed by placing a sheet of blotting-paper between the letter and the leaf of the copying-book, and then gently rubbing the hand over the whole.

C. H. B.

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## General and Physical Chemistry.

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**Chemical Action of Light.** By G. LEMOINE (*Compt. rend.*, **93**, 514—517).—The author compares the action which light has on chemical change with that exercised by heat. Isomeric modifications of sulphur and phosphorus are produced by the action of light. Styrolene is transformed into metastyrolene when it is heated to 200°: if it is exposed to the sun for 20 or 30 days in a sealed tube, the same change takes place. Chloral is polymerised by sunlight; but the heat generated is sufficient to induce decomposition. When acetylene is exposed to light for three years, it acquires a greenish tint, and undergoes a condensation of 7 per cent. Perfectly dry cyanogen and pure turpentine are unchanged. Many of the reactions induced by light proceed when the substances are in solution: solutions of sulphur, phosphorus, and styrolene are transformed. Hydriodic acid gas is decomposed by sunlight, but its solution remains colourless. Silver chloride dissolved in ammonia is not acted on by light. When styrolene is heated at 100° in sealed tubes in the dark, it becomes solid; the same change takes place in the light at 25°.

The blue rays effect all chemical changes sooner than the other colours. The red rays will, in course of time, produce the same effect as the blue ones do in a short time.  
J. I. W.

**Action of Air in rendering the Flame of the Bunsen Lamp more Luminous.** By R. BLOCHMANN (*Ber.*, **14**, 1925—1928).—This paper is merely an answer to Heumann's criticisms (*Abstr.*, 1881, 773) on the author's experiments on conditions of luminosity and non-luminosity of the Bunsen burner.

The author does not, however, bring forward any new experiments to support the views which were put forward by him in a former communication (*Annalen*, **207**, 167).  
V. H. V.

**Non-luminosity of the Flame of the Bunsen Lamp.** By K. HEUMANN (*Ber.*, **14**, 2210—2211).—This paper is merely a controversial reply to the criticisms of Blochmann.  
V. H. V.

**Spectrum of Hydrogen and Acetylene.** By A. WÜLLNER (*Ann. Phys. Chem.* [2], **14**, 355—362).—In 1868 the author described (*Pogg. Ann.*, **135**, 497) the spectrum of hydrogen; but, subsequently, Ångström (*ibid.*, **144**, 300) stated that the lines mentioned by Wüllner were due to the presence of a hydrocarbon; it was, however, afterwards shown by the author (*ibid.*, **144**, 481) that Ångström's supposition was incorrect. More recently still, Ciamician (*Wien. Ber.*, **82**, 425) has stated that the lines ascribed to hydrogen by the author are really due to acetylene. Wüllner has, therefore, carefully studied the spectrum of acetylene, and finds that it is quite distinct



from that which he observed in the case of hydrogen, inasmuch as it shows the carbon channelings characteristic of carbon spectra; and, further, in the red, orange, and yellow portions of the spectrum, it resembles more nearly those of carbonic anhydride and carbonic oxide than that of hydrogen, whilst in the case of ethylene and marsh-gas this part of the spectrum is very similar to that of hydrogen.

The spectrum of acetylene is not of very long duration, as the gas gradually undergoes decomposition, with separation of carbon, the greenish-white light being at the same time replaced by a reddish-white, the spectrum finally assuming almost exactly the same appearance as that of hydrogen. The decomposition of the acetylene takes place much more rapidly when once the walls of the tube and the electrodes have become covered with a thin film of deposited carbon.

In his first paper above referred to, the author described a second line-spectrum, which was observed when the hydrogen was examined under the lowest possible pressure; under these circumstances the light suddenly assumed a green colour, and gave a spectrum consisting of six groups of lines in the green. As this phenomenon was not observed in the case of any other gas than hydrogen, it was ascribed to the presence of the latter gas. He now finds, however, that it is due to the volatilisation of the glass of the vacuum-tube. T. C.

**Spectra of Carbon Compounds.** By A. WÜLLNER (*Ann. Phys. Chem.* [2], **14**, 363—366).—A criticism on a paper by Wesendonck (*Monatsb. d. Berl. Acad.*, 1880, 791) in reference to this subject.

T. C.

**Spectroscopic Examination of Essential Oils.** By W. N. HARTLEY and A. K. HUNTINGTON (*Proc. Roy. Soc.*, **131**, 1—26).—This paper contains descriptions and diagrams of the absorption-spectra of numerous essential oils belonging to the terpene family, the conclusions with regard to which are summarised as follows:—

1. Terpenes, with the composition  $C_{10}H_{16}$  (oils of turpentine, orange, nutmeg, myrtle, and several others), possess in a high degree the power of absorbing the ultra-violet rays of the spectrum, although they are inferior in this respect to benzene and its derivatives.

2. Terpenes with the composition  $C_{15}H_{24}$  (hydrocarbons from rose-wood, cubebs, calamus, cascarilla, patchouli, and cloves), have a greatly increased absorptive power.

3. Neither the terpenes themselves nor their oxides or hydrates exhibit absorption-bands, under any circumstances, when pure, but always transmit continuous spectra.

4. Isomeric terpenes transmit spectra which differ from one another in length, or show variations on dilution.

5. Dilution with alcohol enables the presence of bodies of the aromatic series to be detected in essential oils, and even, in some cases, allows of an approximate estimation of the amounts of these substances present.

H. W.

**Influence of Molecular Grouping in Organic Bodies on their Absorption in the Infra-red Region of the Spectrum.**

By W. DE W. ABNEY and R. FESTING (*Proc. Roy. Soc.*, **31**, 416) —The source of light used in this research for obtaining a continuous spectrum was the incandescent positive pole of an electric light, the electricity being generated by a Gramme machine. The light was passed through tubes containing the liquids, and the absorption was photographed in the infra-red region. It was found that a large number of lines formed in hydrocarbons containing no oxygen are common to substances containing hydrogen and no carbon, *e.g.*, hydrochloric acid, ammonia, and chloroform, and that in carbon tetrachloride and carbon bisulphide no lines or bands are met with. By this eliminating process it is inferred that the presence of lines is due to the hydrogen in the bodies. The experiments show that the termination of the bands in liquids containing carbon, hydrogen, and oxygen, corresponds with the position of these hydrogen lines: hence it appears probable that the bands are in reality a blocking out of radiation between two hydrogen lines.

The most important conclusion deduced from these observations is that each organic radicle has its own definite absorption in the infra-red, and that such a radicle may be detected in a more complex body. It also seems possible that the hydrogen which is replaced may be distinguished by a comparison with other spectra. Coincidences are also pointed out of some of the lines obtained, the absorption-spectra of the hydrocarbons, and the spectra of bodies containing no carbon with solar lines, from which the authors conclude that at present it is not safe to infer that such lines in the solar spectrum are not necessarily due to water. Whether the lines mapped are due to hydrogen or not, it is perfectly evident that every organic body has a definite absorption-spectrum, which connects it with some series. The full paper in the Philosophical Transactions contains tables and maps of the bands and lines found in 51 compounds, including alcohols, ethers, and acids of the paraffin or fatty series, together with benzene and several of its haloïd, nitro-, and amido-derivatives. H. W.

**Absorption-spectra of Cobalt Salts.** By W. J. RUSSELL (*Proc. Roy. Soc.*, **31**, 51—54; and **32**, 258—272).—Anhydrous cobalt chloride,  $\text{CoCl}_2$ , in the fused state gives exactly the same absorption-spectrum in whatever way it may have been prepared. The bromide gives a similar spectrum, but its position is different, being nearer to the red than that of the chloride. By fusing cobaltous chloride with potassium chloride a greenish-blue mass is obtained, which gives a spectrum entirely different from that of the cobalt chloride alone. The same spectrum is exhibited by the mass formed on fusing cobalt chloride with the chloride of sodium or of zinc, and by the solution of cobalt chloride in ethylic or amyl alcohol, the saline ethers, glycerol, or hydrochloric acid, or in fact in any liquid which dissolves the cobalt chloride freely without combining with it. Hence it appears that this spectrum must be that of cobalt chloride itself, the salt being, however, brought by the act of solution into a molecular condition different from that which it has when fused alone, and therefore exhibiting an altered spectrum. The spectrum obtained in the hydrochloric acid solution is remarkable for its persistence

under varying circumstances, and for affording a reaction of great delicacy.

Bromide and iodide of cobalt, when fused with bromide and iodide of potassium respectively, give results similar to those of the chloride; but the bands in the spectrum of the bromide, and still more those of the iodide, are nearer to the red than the corresponding bands of the chloride.

Hydrochloric acid as a solvent for cobalt chloride differs in one respect from all other solvents yet examined, namely, that the spectrum is the same, whether the quantity of cobalt dissolved in it be large or small, whereas with anhydrous alcohol, for instance, a saturated or nearly saturated solution gives the spectrum above mentioned; but a dilute solution containing about 20 g. of the chloride in 100 c.c. alcohol gives a somewhat different spectrum, a new band appearing, while others which were present fade out. With only about 0.08 g. chloride in 100 c.c. alcohol an entirely different spectrum is obtained, but any degree of dilution beyond this is not attended with further change. With other liquids which dissolve the cobalt salt freely, a similar series of changes occurs; but with liquids in which the chloride is much less soluble, only the first (or most dilute) stage, or the first and second, are obtainable; dry ether, for example, yields only a spectrum corresponding with the first stage. With glacial acetic acid, in which the cobalt chloride is more freely soluble, the first and second stages may be obtained. If the dry chloride in fine powder be shaken up with a liquid in which it is insoluble, such as carbon tetrachloride, then only a spectrum similar to that of the fused chloride is visible.

Anhydrous cobalt chloride dissolved in water forms a pink solution, which, when it contains from 0.1 to 25 g. of the salt in 100 c.c. water, gives only a wide absorption-band, shading off on both sides, the spectrum being the same whether a short column of the strong solution or a proportionally large column of the dilute solution be examined, so that within these limits the same compound appears to exist in the solution. If, however, the solution approaches saturation (32 g.  $\text{CoCl}_2$  in 100 c.c. water at  $16^\circ$ ) another spectrum becomes visible, viz., that of the dissolved chloride already mentioned: hence the anhydrous chloride appears to be capable of existing in an aqueous solution. The action of heat and that of bodies capable of combining with water on aqueous solutions of cobalt chloride are identical, both tending to destroy the broad absorption-band of the hydrate, and to form the banded spectrum of the dissolved anhydrous chloride.

The very characteristic spectrum of cobaltous oxide is well shown by the precipitate formed on adding potash or soda in excess to any cobaltous salt. With ammonia as precipitant, a somewhat simpler spectrum is obtained. A piece of cobalt glass gives a spectrum apparently similar to that formed by the precipitate with potash and soda: hence the extra band visible in these cases, and not when ammonia is used, is probably due to a compound of the alkali and cobalt.

If the oxide be precipitated in solutions containing an excess of the cobalt salt, or even if the precipitated oxide be warmed or shaken

up in the cold with a solution of cobalt chloride, an oxychloride is formed, which gives a different spectrum, the formation of this compound and its decomposition by water being well traced in the varying spectra producible from it, and going hand in hand with the chemical changes which occur. The spectroscopic appearance indicates that the blue precipitated oxide is not a hydrate, but the alteration of colour which takes place shows that it readily undergoes change.

Aqueous solutions of cobaltous bromide and iodide are affected by alkalis similarly to the chloride, and, as in former cases, the iodide spectrum is always nearer the red end than the corresponding bromide spectrum, and the bromide spectrum nearer to that end than the chloride spectrum. The cobalt salts of the oxygen-acids do not give sharp-banded spectra, like those of the haloid salts, but only a large shading-off absorption like that of cobaltous hydroxide. H. W.

**Refraction-equivalents of Carbon, Hydrogen, Oxygen and Nitrogen in Organic Compounds.** By J. H. GLADSTONE. (*Proc. Roy. Soc.*, **31**, 327—330).—This paper gives a summary of the author's present views in regard to the refraction-equivalents of these four elements. The figures are always reckoned for the line A of the solar spectrum, the refraction-equivalent being the specific refraction for A multiplied into the atomic weight, or  $P^{\mu_A} \frac{1}{d}$ .

*Carbon* in its compounds has at least three equivalents of refraction, 5.0, 6.0 or 6.1, and about 8.8, the variation appearing to depend on the way in which the atoms are combined. (a.) A single carbon-atom having each of its four units of atomicity satisfied by some other element has a refraction-equivalent not greater than 6, and probably somewhat less. (b.) A carbon-atom having one of its units of atomicity satisfied by another carbon-atom and the remainder by some other element, has the value 5.0, the same as in diamond. This is also the case when two of its units of atomicity are satisfied by carbon-atoms. The majority of organic compounds fall into this category. (c.) When a carbon-atom has three of its units of atomicity satisfied by other carbon-atoms, its refraction-equivalent is 6.0. This is most strikingly seen in benzene (refr. eq. = 43.7), in which, reckoning 1.3 for each hydrogen-atom, we find for each carbon a value slightly less than 6.

Styrolene or cinnamene,  $C_8H_8$  (57.3), gives a similar value.

There are other organic compounds—the amylene and allyl compounds for example—in which the higher value is exhibited, not by all the carbon-atoms, but only by those which may be supposed to be united to others by double bonds. According to Brühl, the refraction-equivalent of these carbon-atoms is 6.1.

When a carbon-atom has all its four units of atomicity satisfied by other carbon-atoms, each of which has the higher value 6.0 or 6.1, its refraction-equivalent is greatly raised. Such is the case in naphthalene,  $C_{10}H_8$  (refr. eq. 75.1), naphthol,  $C_{10}H_8O$  (79.5), phenanthrene,  $C_{12}H_{10}$  (108.3), and pyrene,  $C_{16}H_{10}$  (126.1), in which, even if all the carbon-atoms are supposed to have the value 6.1, the refraction-equivalent of the compound will not be fully accounted for. Provi-

sionally, the author estimates the refraction-equivalent of this highest carbon at 8.8. Several other bodies, as anthracene, anethol, furfuraldehyde and cinnamyl hydride; appear from their abnormally high refraction to contain carbon in this last condition.

*Hydrogen*.—The general evidence with regard to this element in organic compounds tends to show that it has only one refraction-equivalent, viz., that originally assigned to it by Landolt, 1.3.

*Oxygen*.—Brühl first showed that oxygen in organic compounds has two refraction-equivalents, namely 3.35 when it is doubly linked to a carbon-atom, and 2.76 in hydroxyl, and where the oxygen is united to two other atoms. This conclusion is deduced from experimental data, but there are some anomalous cases. Thus in water,  $H_2O$  (5.9) the oxygen appears to have the higher value 3.3, notwithstanding its attachment to two hydrogen-atoms, while in  $CH_4O$  (13.1),  $C_2H_6O$  (20.8), as well as in higher monatomic alcohols, and in ethylene alcohol,  $C_2H_6O_2$  (23.7), and glycerol,  $C_3H_8O_3$  (33.9), the oxygen is not 2.76 but 2.9 or 3.0.

*Nitrogen* has two values, 4.1 and 5.1 or thereabouts, the lower value being that which was originally deduced from cyanogen and the metallic cyanides, and appears to be generally confirmed by the observations on organic cyanides and nitrils. The higher value is deduced from the author's observations on organic bases and amides, such as diethylamine (39.4), triethylamine (54.6), formamide (17.4), &c.

The determination of the value of nitrogen in nitro-derivatives presents peculiar difficulties, the observations not being accordant. Even if the value of  $NO_2$  were determined with certainty, it would still not be easy to say how much should be assigned to the oxygen, especially when it is remembered that the refraction of the analogous elements, phosphorus and arsenic, is very materially altered by combination with oxygen.

H. W.

**Electrolysis of Water.** By D. TOMMASI (*Compt. rend.*, **93**, 638—639).—The author finds that a zinc-copper or zinc-carbon element immersed in dilute sulphuric acid, does not decompose water if the two electrodes are made of platinum. If, however, the positive electrode is a metal which under the influence of a voltaic current is capable of combining with oxygen, the single element is able to decompose the water.

J. I. W.

**A Pile with Manganese, forming Salts which can be Utilised or Regenerated.** By J. ROUSSE (*Compt. rend.*, **93**, 546—547).—The author replaces the zinc of a Bunsen element by ferromanganese (85 per cent.). The electromotive force is equal to that obtained with amalgamated zinc. The advantage of the substitution is that the salts produced can be made use of. The exciting liquids employed are dilute sulphuric and concentrated nitric acids. Potassium permanganate can be employed instead of the nitric acid. When permanganate is used, the salts produced are sulphate and nitrate of manganese and potassium. The author converts the manganese salts into sesquioxide, and then again into permanganate.

J. I. W.

**Secondary Piles.** By J. ROUSSE (*Compt. rend.*, **93**, 545—546).—The author states, that in order to construct a secondary pile, it is only necessary to procure for the negative pole a metal which absorbs hydrogen when placed in a favourable medium, and for the positive pole one which can take up oxygen. He has constructed piles with the following composition:—

Negative pole.	Positive pole.	Liquid.	Remarks.
1. Palladium .....	Sheet lead .....	10 p. c. $\text{H}_2\text{SO}_4$ ..	Very powerful.
2. Thin sheet of iron	Sheet lead alone or covered with litharge	50 p. c. solution of $(\text{NH}_4)_2\text{SO}_4$	
3. Sheet iron .....	Ferromanganese .....	40 p. c. solution of $(\text{NH}_4)_2\text{SO}_4$	

J. I. W.

**A Convenient Form of Air Thermometer for Temperatures above 360°.** By L. W. ANDREWS (*Ber.*, **14**, 2116—2120).—This instrument consists of a thermometer tube and bulb (1 c.c. capacity). The tube is bent twice at right angles, and the upper end is widened out and fitted with a well ground stopcock, connected by means of india-rubber tubing and a T-piece with a manometer also fitted with a stopcock at the bottom, and with an india-rubber reservoir. The capillary tube and bulb are filled with dry air, the other parts of the apparatus with mercury. For use, the mercury meniscus is adjusted to a certain point (the point where the thermometer tube commences to widen) by pressing the rubber reservoir, and the height of the mercury in the manometer read off; if the bulb is now heated, the mercury will be depressed; to read the temperature reached, the mercury is readjusted to the point, and the manometer reading taken; from the difference in the pressure thus determined the temperature can be calculated.

A special arrangement is used for pressing the reservoir.

With this apparatus the author found:—

Boiling point of sulphur 447° (Regnault 448.4°).

“ “ phosphorus pentasulphide 527° (Hittorf 530°).

“ “ phenyl phosphate 407°. D. A. L.

**Heat of Formation of Water.** By A. SCHULLER (*Ann. Phys. Chem.* [2], **14**, 226—232).—A reply to the criticisms of v. Than (*Wied. Ann.*, **13**, 84, 105) on a paper by the author and v. Wartha (*ibid.*, **2**, 371), with reference to this subject. T. C.

**Expansion of Water by Heat.** By P. VOLKMANN (*Ann. Phys. Chem.* [2], **14**, 260—279).—An historical account is given of the various determinations which have been made of the expansion of water by heat, from which it is shown that the determinations have never been made directly, and that in all, the expansion of glass has had to be allowed for. In consequence of this, the peculiar behaviour of glass may possibly have introduced a slight error into all the values obtained. T. C.

**Vapour-tension of Mixed Liquids.** By D. KONOWALOFF (*Ann. Phys. Chem.* [2], **14**, 219—226).—In continuation of his former work (*Wied. Ann.*, **14**, 34, 1881), the author finds that if a mixture of several solid and liquid bodies forms two layers, the vapour-tension and composition of the vapours from the two layers are equal. T. C.

**On the Critical Point.** By W. RAMSAY (*Proc. Roy. Soc.*, **31**, 194—205).—The experiments described in this paper were undertaken with the view of determining the difference of behaviour of two pure compounds (benzene and ether), and a mixture of the two, at high temperatures and under great pressure. The mode of working is described, and the relations of pressure, temperature, and volume determined by the experiments are given in tables and graphically represented by isothermal curves.

From the results obtained the author draws the following general conclusions:—

1. That a gas may be defined as a body whose molecules are composed of a small number of atoms. 2. A liquid may be regarded as formed of aggregates of gaseous molecules forming a more complex molecule; and 3. Above the critical point, the matter may consist wholly of gas if a sufficient volume be allowed; wholly of liquid if that volume be diminished sufficiently; or of a mixture of liquid and gas at intermediate volumes. Such a mixture is, physically speaking, homogeneous, in the same sense as a mixture of oxygen and hydrogen gases may be termed homogeneous; but it is chemically heterogeneous, inasmuch as it consists of molecules of two different natures. When prevented from mixing by the interposition of a capillary tube between the two, the liquid and gas retain their several properties.

H. W.

**Limit of the Liquid State.** By J. B. HANNAY (*Proc. Roy. Soc.*, **31**, 520—522).—In this paper, the author discusses the question whether the liquid state extends above the critical temperature, or whether it is bounded by an isothermal line passing through the critical point. The critical temperature and pressure of a liquid having been determined accurately, a quantity of a gas insoluble in the liquid was compressed over it, and the critical temperature again determined under increased pressure. When the densities of the two bodies, *e.g.*, alcohol and hydrogen, differ widely, the gas does not lower the critical temperature, as is the case with carbonic anhydride and air, whose densities are much nearer to that of the liquid, but simply acts as a spring, against which the upper surface of the alcohol presses, and thus presents a surface free for observation at pressures far above that of the vapour of the liquid. When the liquid passes the critical temperature at any pressure, the meniscus is lost, and the liquid diffuses freely into the superincumbent gas; but this does not occur at temperatures below the critical, except where very high pressure has made the gas appreciably soluble in the liquid. Thus the curve of vapour-tension, that is, the curve representing the temperatures at which a given pressure will produce liquefaction, suddenly becomes isothermal at the critical point, and passes along the co-ordinate denoting the critical temperature.

As surface-tension is the only property by which the liquid state can be known, the capillary height of the liquid at various temperatures was next determined. The capillary height becomes zero at the critical temperature, and this is the case whether the pressure is the critical pressure or a higher one. The surface-tension is lowered a little by the action of the compressed hydrogen, but the change of capillarity follows that of the liquid alone very closely, and the capillarity sinks to zero a few degrees below the critical temperature. *Nitrogen* may be substituted for hydrogen with the same results; also with various liquids, as carbon bisulphide, carbon tetrachloride, and methyl alcohol.

From these results the author concludes that matter may be classified under four states:—1. The *gaseous*, which exists from the highest temperatures down to an isothermal passing through the critical point, and depending entirely on temperature or molecular velocity. 2. The *vaporous*, bounded on the upper side by the gaseous, and on the lower by absolute zero, and depending entirely on the length of the mean free paths. 3. The liquid. 4. The solid. H. W.

**Affinity Values of Fluorine with the Metals, as deduced from the Law of Smallest Volumes.** By W. MÜLLER-ERZBACH (*Ber.*, 14, 2212—2215).—For the compounds of the halogens, oxygen, and sulphur with the metals, the author has found that the greater the affinity values of their constituents, the greater the contraction in their formation; and in the formation and double decomposition of the chlorides of the metals, greater condensation is correlated with greater affinity values (*Abstr.*, 1881, 219), so that generally the elements tend to arrange themselves ultimately in those forms of combination which occupy the smallest volumes. The exceptions to this general law are but few, and these occur only in the case of compounds, the heat-changes in formation of which have not been satisfactorily examined. From this law of "smallest volumes," the author in the present communication endeavours to deduce the relative affinity values of fluorine with the metals, and arranges them in the following series:—Rb, K, Na, (Li, Ba, Sr), Ca, Mg, Pb, Ag, and Al, As (the affinity values of Li, Ba, Sr with fluorine were found to be approximately equal). This series agrees with that of Gmelin, deduced from experiments on double decomposition. V. H. V.

**Lecture Experiments.** By M. ROSENFELD (*Ber.*, 14, 2102—2105).—*Demonstration of chemical change of weight of bodies by chemical processes.* For this purpose, the author suggests the use of a small hydrometer, made with a glass body (from a saccharometer) and a neck of thick wire, 10 cm. long, and 1 mm. thick, to the upper end of which a small glass dish (the bottom of a test-tube) is attached; a piece of platinum foil (or in case the substance attacks this metal, a thin porcelain plate), placed on the dish, serves as a support for the substance under examination. When used, the apparatus is so adjusted, that with about a gram of substance it sinks so far in the water as just to let the wire dip in a little. In this position, an increase of .02 gram in weight is readily seen. For substances of which the products of oxida-



tion, &c., are gaseous, a Nicholson's hydrometer may be used, a small absorption-tube being placed on the plate.

*Combustion of Ammonia in Oxygen.*—This is conducted in a flask, fitted with a cork bored with two holes, through one of which a tube bent at right angles passes almost to the bottom of the flask, and into the other a drying tube is fitted having a metal tube, 2 mm. diameter, at the upper end; the drying tube is filled with soda-lime, supported on wire gauze and cotton wool. For use, the flask is partially filled with strong ammonia, the liquid is boiled, and the cork is put in. Oxygen passed through the right-angled tube, bubbles through the liquid, and the mixture of gases can be burnt at the opening of the metal tube. The flame is very hot; it makes lime glow strongly, and melts even tolerably thick platinum wire.

*Synthesis of Water.*—For this experiment a glass T-piece is used, having a smaller glass tube, tipped with platinum, passing through the horizontal part; the hydrogen is sent in through this tube and set on fire, the oxygen being supplied through the side tube of the T-piece, and the whole fitted in a flask; the drops of water then condense in the inside.

D. A. L.

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## Inorganic Chemistry.

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**Preparation and Application of Hydrobromic Acid.** By A. HARDING (*Ber.*, **14**, 2085—2092).—An apparatus is described for the preparation of hydrobromic acid synthetically. The hydrogen and bromine, the former in slight excess, are passed together through a glass tube (1 m. long, 7 mm. diameter), surrounded by another glass tube through which a current of steam circulates, and thence into a platinum tube (14 cm. long and 12 mm. diameter) containing a platinum spiral heated to redness. The hydrobromic acid thus formed is collected in water in thin flasks, cooled by a stream of water; any free bromine is removed from the escaping gas by passing it over a tube filled with antimony. With tubes of the above dimensions, 1 kilo. of concentrated hydrobromic acid can be made in an hour. The organic matter present in commercial bromine may be conveniently removed by sending the bromine-vapour over red-hot manganic oxide.

Hydrobromic acid dissolves all simple sulphides, both natural and artificial, with evolution of sulphuretted hydrogen. The author recommends a method for estimating sulphur either in sulphides or free sulphur by means of hydrobromic acid. The apparatus employed is fully described, into which the substance is introduced along with small pieces of amalgamated copper wire and some mercury, the air being expelled by a current of hydrogen, and hydrobromic acid run in. The tube is then carefully warmed until all the substance is dissolved, when more hydrobromic acid is introduced, and the whole well boiled to drive off the hydrogen sulphide, the last traces being removed by a current of hydrogen. The loss in weight is the hydrogen sulphide

evolved. This method is based on the fact that the sulphur in a metallic sulphide or in free sulphur is completely converted into hydrogen sulphide when these substances are treated with hydrobromic acid in presence of amalgamated copper. Several results are given, which agree very well with one another. Each estimation takes from  $1\frac{1}{2}$  to 2 hours. Hydrobromic acid dissolves mercury, copper, and lead with evolution of hydrogen. D. A. L.

**Action of Sulphurous Anhydride on Nitric Oxide in Presence or Absence of Oxygen.** By G. LUNGE (*Ber.*, **14**, 2196—2202).—The author has made a series of experiments in his gas analysis apparatus on the action of nitric oxide and nitrous acid, in order, if possible, to offer some better explanation of the chemical changes which take place in the lead chambers. The mixture of oxygen, nitrous and nitric oxides, and nitrogen resulting from the experiments were analysed according to the methods proposed by the author (see “Analytical Chemistry”). Attention is also drawn to the difficulty in obtaining nitric oxide and oxygen absolutely free from nitrogen derived from the air; this impurity, however, was taken into consideration in the calculation of the results.

*Experiments*:—(i) Dry nitric oxide and dry sulphurous anhydride have no action on one another either at ordinary temperatures or at  $50^\circ$  or  $100^\circ$ ; (ii) gas containing 32.1 per cent. NO and 69.9 per cent.  $\text{SO}_2$  was placed in contact with water; a violent reaction took place, all the nitric oxide was converted into nitrous oxide, but no nitrogen was formed; (iii) a sample of gas containing excess of nitric oxide (10 per cent. : 30 per cent. NO :  $\text{SO}_2$ ) was treated in a similar manner; a considerable portion of the nitric oxide was reduced to nitrous oxide. A series of experiments were then made, dilute sulphuric acid (sp. gr. 1.45) being substituted for water. The author confirms the observations of Weber (*Pogg.*, **130**, 129) that no reduction of nitric to nitrous oxide takes place; but on using more dilute sulphuric acid (sp. gr. 1.32), there was a very slight reduction of the nitric oxide. As these experiments do not satisfactorily represent the conditions which obtain in the lead chambers, a series of experiments were made, using a mixture of nitric oxide, sulphurous anhydride, oxygen, and water; but the author puts forward the results with a certain reserve, owing to the great experimental difficulties in the manipulation of such a gaseous mixture. The author, however, arrives at the practical result that, even with an excess of oxygen, the higher oxides of nitrogen are partially reduced to nitrous oxide in the presence of water and sulphurous acid. When a mixture of sulphurous anhydride, nitric oxide, oxygen, and nitrogen was placed in contact with sulphuric acid, no decided quantity of nitrous oxide was formed. V. H. V.

**Ammonium Tribromide.** By H. W. B. ROOZEBOOM (*Ber.*, **14**, 2398—2400).—When bromine is added to a concentrated aqueous solution of ammonium bromide, a considerable rise in temperature is produced. The solution slowly deposits large prismatic crystals resembling potassium dichromate in colour. They have the composition  $\text{NH}_4\text{Br}_3$ . On exposure to the air, the bromine escapes. Ammonium

tribromide appears to combine with a molecule of bromine, but the pentabromide has not yet been isolated. W. C. W.

**Note on a Phosphorus Oxyiodide.** By S. BURTON (*Am. Chem. J.*, 3, 280).—This body is found in the residue left in the retort in the preparation of ethyl iodide, and may be separated by treating the residue with water, filtering, and evaporating, whereupon it is deposited in red granular crystals, which may be purified by recrystallisation. It dissolves readily in water, alcohol, and ether, forming colourless solutions. It melts at  $140^{\circ}$ , and at a higher temperature gives off yellowish vapours, which blue starch-paper, and condense on a cold surface as a yellowish-red crystalline deposit, exhibiting all the characters of the original substance, which therefore partly sublimes unaltered. By analysis, it gave numbers agreeing with the formula  $I_6P_3O_8$ . A similar body has been observed in the residue from the preparation of fuming hydriodic acid: its composition appears to be  $I_2PO_2$  or  $I_8P_4O_8$ . This body appears also to be formed in the preparation of methyl iodide. H. W.

**The Anhydride of Phosphorous Acid.** By R. REINITZER (*Ber.*, 14, 1884—1887).—It is stated in all text-books that the product of combustion of phosphorus in a limited supply of oxygen is the anhydride of phosphorous acid. But Leverrier observed that when water is gradually added to the product, a deep golden liquid is obtained, which coagulates on heating to  $80^{\circ}$ ; and on adding excess of water, a red flocculent precipitate is obtained without the intermediate formation of the yellow solution. It is generally considered that this red precipitate is amorphous phosphorus which has been protected by a layer of phosphorus trioxide; but the author observed that the oxide, although purified by sublimation from all adhering traces of phosphorus, yet formed, when heated with water, a considerable quantity of the red precipitate. Thus it is probable that Wislicenus' interpretation of this phenomenon is partially correct, and that the phosphorous anhydride is decomposed according to the equation  $5P_2O_3 = 3P_2O_5 + P_4$ , the red precipitate being amorphous phosphorus. A study of the golden aqueous solution described above showed that the phosphorus compound contained in it was a *colloid substance in which the relation of phosphorus to oxygen was as 2:3, and to which can be assigned the preliminary formula*  $mP_2O_3 + nH_2O$ . At the same time it is not correct to regard the product of combustion of phosphorus as the anhydride of phosphorous acid, for its *aqueous solution is perfectly neutral and contains a colloid*. There can be no doubt that the action of phosphorus trichloride on phosphorous acid in sealed tubes at  $70^{\circ}$  yields the same body that is formed by the burning of phosphorus under water with oxygen (Vogel), by the oxidation of phosphorus, by the action of aqueous iodic and periodic acids on phosphorus (Bénckisen), and by the combustion of phosphorus with ammonium nitrate (Marchand). It further appears that the composition of the red precipitate is very variable, and that it contains oxygen and hydrogen, and is probably a derivative of the solid phosphoretted hydrogen  $n(P_4H_2)$  in which the hydrogen is more or less replaced by oxygen. V. H. V.

**Chemistry of the Superphosphates.** By E. ERLÉNMEYER (*Ber.*, **14**, 1869—1870).—The author has observed that the retrogression of phosphoric acid in the phosphorite superphosphates is due mainly to the iron present in these manures, and that the influence of aluminium becomes perceptible only after very long keeping. By exposure of the monoferro- and monoferri-phosphate to the air, the insoluble Winckler's salt is formed. On studying the solubility of Winckler's salt in ammonium citrate solution, it was found that the acid citrate solution dissolved the least, and the ammoniacal solution dissolved the greatest quantity of phosphoric anhydride.

The precipitation of oxalic acid as magnesium oxalate, by magnesium mixture, is entirely prevented by ammonium citrate, but if large quantities of ammonium chloride are added the oxalate is still precipitated. On the behaviour of the phosphates to ammonium citrate solution, the author has based a method of analysis for calcium phosphate and superphosphates.

V. H. V.

**Action of Sulphur on Alkaline Sulphides in Dilute Solutions.** By FILHOL (*Compt. rend.*, **93**, 590—591).—The author shows that when a very dilute solution of an alkaline sulphide, such as is found in a mineral water, is boiled with sulphur, a reaction takes place between the sodium hydrosulphide and hydroxide, a polysulphide of sodium being formed:  $\text{NaHS} + \text{S} + \text{NaOH} = \text{Na}_2\text{S}_2 + \text{H}_2\text{O}$ .

J. I. W.

**Barium Aluminate and Basic Halogen Salts of Barium.** By E. BECKMANN (*Ber.*, **14**, 2151—2158).—On dissolving freshly precipitated alumina with a sufficient quantity of baryta solution, and evaporating the liquid, asymmetrical transparent crystals of a compound,  $\text{Al}_2\text{O}_3 \cdot 2\text{BaO} + \text{Aq}$ , separate out. On suitably modifying the conditions of formation, other compounds of barium and aluminium oxides, viz.,  $\text{Al}_2\text{O}_3 \cdot \text{BaO} + \text{Aq}$ , and  $\text{Al}_2\text{O}_3 \cdot 3\text{BaO} + \text{Aq}$  are obtained. These compounds retain a considerable portion of their water of hydration even when they are heated with potassium dichromate to its melting point, a condition under which baryta is rendered anhydrous.

On adding baryta-water in excess to a solution of aluminium chloride, the precipitated alumina is dissolved, and on evaporating a chlorine-compound,  $\text{Al}_2\text{O}_3 \cdot \text{BaO} \cdot 3\text{BaCl}_2 + \text{Aq}$ , crystallises out in microscopic crystals. This substance may also be obtained when a cold concentrated solution of the barium aluminate,  $\text{Al}_2\text{O}_3 \cdot 2\text{BaO} + \text{Aq}$ , is saturated with barium chloride. Under other conditions a compound of the formula  $\text{Al}_2\text{O}_3 \cdot \text{BaO} \cdot \text{BaCl}_2$ , can be prepared. Similar bromine and iodine compounds,  $\text{Al}_2\text{O}_3 \cdot \text{BaO} \cdot \text{BaBr}_2 + \text{Aq}$ ;  $\text{Al}_2\text{O}_3 \cdot \text{BaO} \cdot \text{BaI} + \text{Aq}$ , are also described. When a current of carbonic anhydride is passed into an aqueous solution of these substances, the aluminium and a portion of the barium is precipitated, only the halogen salt remaining in solution.

The author then made a series of experiments in order to determine the precise conditions under which a barium oxychloride is formed. By the action of baryta on barium chloride in concentrated hydrochloric acid, an oxychloride of composition  $\text{BaCl}(\text{OH}) + 2\text{H}_2\text{O}$

was obtained (cf. André, Abstrs., 1881, 979). A similar oxybromide,  $\text{Ba}(\text{OH})\text{Br}$ , and oxyiodide,  $\text{Ba}(\text{OH})\text{I}$ , are described. The author proposes to continue his researches.

V. H. V.

**Crystallised Copper Sulphide Formed from Ancient Coins in Hot Springs.** By DAUBRÉE (*Compt. rend.*, 93, 572—574).—At Flines les Roches, in canton Douai, is a large hot spring known as the Mer de Flines. Coins and other bronze articles which have been found in it are observed to be encrusted with a crystalline substance which has evidently been formed at their expense. It is a black pellicle 2 mm. in thickness. On the exterior is an extremely thin coating of chalkopyrite, but the greater part of the encrustation consists of a variety of chalkosine known as Cupreine. Individual hexagonal crystals are found here and there in the centre of the mass.

J. I. W.

**Iodine-compounds of Lead.** By A. DITTE (*Ann. Chem. Phys.* [5], 24, 226—253).—*Action of Lead Iodide on Alkaline Iodides.*—When lead iodide is brought into a solution of potassium iodide, a small quantity, increasing with the proportion of alkaline iodide, dissolves; but as soon as the liquid attains a certain degree of concentration, white crystals are deposited in place of the yellow ones. The former are decomposed on adding water or by elevation of temperature; if however the liquid contains much potassium iodide, the decomposition is incomplete, and the hot filtered solution deposits slender needles on cooling. They have probably the composition  $\text{PbI}_2 \cdot \text{KI} + 4\text{H}_2\text{O}$ , and when heated they lose water and become yellow. Absolute alcohol produces the same effect. They are decomposed on addition of water. The author describes in detail the decomposition of the double salt by water, and also shows under what circumstances it is formed in mixed solutions of the two constituents.

*Action of Lead Oxide on Potassium Iodide, and Action of Potash on Lead Iodide.*—Lead hydroxide is immediately attacked by a solution of potassium iodide, and, if the latter is in excess, it changes the oxide into a white substance, faintly tinted with yellow. This, when left for several days in the liquid in which it has formed, becomes crystalline. The crystals, which are colourless and transparent, have the composition  $2(\text{PbI}_2 \cdot \text{PbO}) + \text{H}_2\text{O}$ . When, however, a hot solution of lead iodide is treated with a concentrated solution of potash, a new compound crystallises out in slender white needles. On being heated it loses water and becomes yellow. Its composition is  $\text{PbI}_2 \cdot 5\text{PbO} + 7\text{H}_2\text{O}$ .

*Action of Lead Carbonate on Potassium Iodide and the Inverse Action.*—Precipitated moist lead carbonate is not attacked at the ordinary temperature by potassium iodide even in a concentrated solution. If, however, a current of carbonic anhydride is passed into the liquid, it is speedily transformed into white needles of the composition  $\text{KI}_2 \cdot \text{PbI} + 4\text{H}_2\text{O}$ . The same compound is obtained by the action of lead iodide on potassium iodide. On treating potassium iodide with an excess of lead carbonate, the compound  $\text{PbI}_2 \cdot \text{PbCO}_3$  is obtained. By the action of lead iodide on potassium carbonate, the salt  $\text{KI}_2 \cdot \text{PbI} + 4\text{H}_2\text{O}$  is formed.

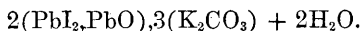
*Action of Lead Peroxide on Iodine.*—When hydrated lead peroxide is added to a solution of iodine in water, the colour disappears in a few hours, lead monoxide and iodic acid being formed.

*Action of Lead Peroxide on Potassium Iodide.*—Lead dioxide decomposes a solution of potassium iodide, however dilute it may be. It forms lead monoxide and potassium hydroxide, and iodine is set free. After some hours brilliant white needles appear in the solution. They consist of the oxyiodide of lead,  $\text{PbI}_2\text{PbO}$ .

*Action of Lead Peroxide on Alkaline Iodides in Presence of Carbonic Acid.*—A mixture of potassium iodide and hydrated lead peroxide, when exposed to the air, is transformed into crystals more rapidly than when kept out of contact with the air. The liquid is found to contain free iodine, and after a few days the lead dioxide is transformed into small yellowish-white needles, of the composition



The salt forms much more quickly if a small quantity of potassium carbonate is added to the solution. If, however, a large quantity of potassium carbonate is present, a new compound, richer in carbonic anhydride, is formed. It has the composition



On passing a current of carbonic anhydride through a mixture of lead dioxide and potassium iodide containing a large excess of the latter, the dioxide changes colour, becoming blue, then green, and finally dissolves entirely. It is replaced by brilliant needles of the double iodide,  $\text{PbI}_2, \text{KI} + 4\text{H}_2\text{O}$ , or, when the liquid contains the proper amount of potassium carbonate and iodide, a compound of this iodide with potassium carbonate,  $\text{PbI}_2, \text{KI}, \text{K}_2\text{CO}_3 + 3\text{H}_2\text{O}$ . By acting with lead dioxide on a mixture of this iodide with an excess of potassium hydrogen carbonate, the double carbonate  $2(\text{PbCO}_3), \text{K}_2\text{CO}_3$  is obtained.

*Blue Lead Iodide.*—Lead hydroxide, when brought in contact with iodine water, becomes yellow, then brown, and finally violet-black. The product is not homogeneous, but contains lead hydroxide coloured with iodine.

In the action of potassium iodide on lead oxide, if the action ceases when there is an excess of lead oxide, a dark violet-coloured mass is obtained. Its composition is variable.

When a solution of potassium hydrogen carbonate is added to potassium iodide with a small quantity of hydrated lead peroxide, the latter undergoes a change and is transformed into a bulky brown substance, which is not homogeneous, but contains some colourless crystals. The brown precipitate becomes green, and finally dark blue, gradually changing into crystals of  $\text{PbI}_2, \text{PbO}, \text{K}_2\text{CO}_3$ : or if the carbonate is in excess it forms the double carbonate  $2\text{PbCO}_3, \text{K}_2\text{CO}_3$ .

J. I. W.

### Vapour-density of Uranium Tetrabromide and Chloride.

By C. ZIMMERMANN (*Ber.*, **14**, 1934—1939).—The author has made determinations of the vapour-density of uranium tetrabromide and tetrachloride, in order to decide between the atomic weight 120, formerly

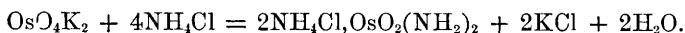
assigned to the metal, or the number 240, proposed by Mendelejeff in accordance with the periodic law.

The tetrabromide is prepared by heating in a current of carbonic acid, laden with bromine-vapour, a mixture of uranoso-uranic oxide and charcoal. The bromide is deposited in the cooler parts of the tube in the form of dark brown to black glistening leaflets, which are converted by heat into a brown vapour, and can be sublimed unchanged. Owing to the very hygroscopic nature of this compound, the most minute precautions are necessary, in order to obtain it in a state sufficiently pure for analysis. Its vapour-density was determined in a V. Meyer's apparatus filled with nitrogen; the mean value of six concordant experiments was 19.46, approximately equal to 19.36, the theoretical number for the vapour-density, if the atomic weight of uranium is 240.

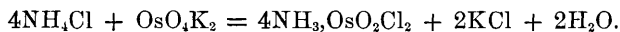
The tetrachloride is obtained together with the pentachloride, by heating a mixture of uranoso-uranic oxide and charcoal in a current of chlorine. By heating the pentachloride in a current of carbonic acid, it can be dissociated into chlorine and the tetrachloride. The mean value of the vapour-density of the tetrachloride from four concordant determinations, was 13.33, the theoretical number ( $U = 240$ ) being 13.21.

These experiments establish the *correctness of Mendelejeff's proposal to double the formerly received atomic weight of uranium.* V. H. V.

**Osmyl-ditetramine.** By WOLCOTT GIBBS (*Am. Chem. J.*, **3**, 233—241).—Frémy in 1874 described a yellow crystalline substance, which he obtained by adding ammonium chloride to a solution of potassium osmate, and to which he gave the formula  $2NH_4Cl, OsO_2(NH_2)_2$ , representing its formation by the equation—



Gibbs, in examining this salt, found that it gave a crystalline compound with platonic chloride, and by double decomposition with silver salts yielded a well-defined crystalline sulphate, nitrate and oxalate: hence he assigned to it the formula  $4NH_2, OsO_2Cl_2 + 2H_2O$ , according to which its formation may be represented by the equation—



Claus afterwards examined this salt, and assigned to it the formula  $4NH_3, OsCl_2 + 2H_2O$ , regarding it as the osmium analogue of well-known compounds of palladium, platinum, iridium, and ruthenium. But if this were the case, it is evident from the last equation that the formation of the salt would be attended with evolution of 2 atoms of oxygen, which, according to the author's experiments, is not the case. According to Claus also the salt contains 2 mols.  $H_2O$ ; but Gibbs finds that when heated for five hours at  $100$ — $154^\circ$ , it gives off only 0.59 per cent. water, whereas a loss of only 1 mol. would require 4.84 per cent.

The author proposes to designate the group  $OsO_2, 4NH_3$  as *osmyl-ditetramine*, to distinguish it from *osmioditetramine*,  $Os, 4NH_3$ , not



yet discovered, which would be analogous to the radicle of the palladium, platinum, ruthenium, and iridium salts above referred to.

*Osmyl-ditetramine Chloride*,  $\text{OsO}_2(\text{NH}_3)_4\text{Cl}_2$ , separates as an orange-yellow crystalline precipitate on mixing the concentrated solutions of ammonium chloride and potassium osmate. It is slightly soluble in cold water, but is quickly decomposed by hot water, with evolution of osmium tetroxide and precipitation of a black powder. Strong hydrochloric acid precipitates it from its solution as a crystalline yellow or orange-yellow powder. It dissolves in hot water containing a little hydrochloric acid, forming a deep orange-yellow solution, from which on cooling it separates in small crystals of a deep brown-yellow colour. It is completely decomposed by ignition, leaving pure metallic osmium as a grey porous mass:  $\text{OsO}_2(\text{NH}_3)_4\text{Cl}_2 = \text{Os} + 2\text{NH}_4\text{Cl} + 2\text{H}_2\text{O} + \text{N}_2$ . This decomposition furnishes the readiest method of obtaining pure metallic osmium. To prevent oxidation, however, the osmium should be heated to a high temperature, and left to cool in a current of hydrogen. Finely divided osmium oxidises readily in the air, giving off vapours of the tetroxide. It likewise exhibits in a remarkable degree the property possessed by spongy platinum, of causing the combination of oxygen and hydrogen, the osmium itself being however oxidised at the same time.

A solution of the chloride gives a fine violet colour with *potassium ferrocyanide*, the reaction affording a very delicate test for osmium. To apply it, the alloy or compound is fused with hydroxide and nitrate of potassium, the fused mass is distilled with nitric acid, and the distillate, after being made slightly alkaline with potash, is reduced to potassium osmate,  $\text{OsO}_4\text{K}_2$ , by a drop of alcohol or a solution of potassium nitrite. A solution of ammonium chloride, nitrate or sulphite is next to be added, and finally the ferrocyanide, whereupon a violet colour will be produced. In this manner, it is possible to detect quantities of osmium too small to be recognised by the characteristic odour of the tetroxide.

*Osmyl - ditetramine platinochloride*,  $\text{OsO}_2(\text{NH}_3)_4\text{Cl}_2, \text{PtCl}_4$ , forms orange-yellow crystals slightly soluble in cold water.

The *sulphate*,  $\text{OsO}_2(\text{NH}_3)_4\text{SO}_4$ , which, like the other salts, is best prepared by pouring a solution of potassium osmate,  $\text{OsO}_4\text{K}_2$ , into a cold strong solution of ammonium sulphate, forms small crystals having a fine orange-yellow colour, somewhat freely soluble in hot, sparingly in cold water. The *nitrate* forms granular orange-yellow crystals paler than the sulphate. It is very unstable, the cold solution soon decomposing, with evolution of  $\text{OsO}_4$ . The *oxalate*,  $\text{OsO}_2(\text{NH}_3)_4\text{C}_2\text{O}_4$ , a very stable salt, forms yellow or orange-yellow crystals, only slightly soluble in cold water.

The constitution of the osmyl-ditetramine compounds may be represented in two ways: the chloride, for example, by either of the formulæ—



the osmium being quadrivalent in the first and bivalent in the second. According to the latter view, the chloride might be expected to form

addition-products by taking up 2 at. iodine, bromine, or other mon-atomic radicle, *e.g.*,  $\text{I}_2\text{Os}[\text{O}(\text{NH}_3)_2\text{Cl}]_2$ ; but no such compounds appear to be capable of existence: hence the first of the above formulæ appears to be the more probable of the two.

Compounds analogous to those above described appear to be formed with certain organic bases. Thus, when a solution of potassium osmate is poured into a cold strong solution of hydrochloride of narcotine, cinchonine, or strychnine, a white precipitate is formed which dissolves readily in dilute hydrochloric acid, the solutions giving precipitates with platinic and auric chlorides. On adding potassium osmate to a solution of luteocobaltic chloride,  $\text{Co}_2(\text{NH}_3)_{12}\text{Cl}_6$ , a buff-coloured precipitate is formed which, on adding dilute hydrochloric acid, becomes orange-yellow and beautifully crystalline. This salt dissolves in cold water without decomposition, but is decomposed on gentle heating. It forms beautiful crystalline salts with the chlorides of gold and platinum. The chlorides of the other cobaltamines likewise react with potassium osmate.

When potassium osmate is mixed with a solution of the chloride of *palladio-ditetramine*,  $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ , an orange-yellow or sherry-coloured solution is formed, from which hydrochloric acid throws down a precipitate of a fine orange-yellow colour. A solution of this salt gives an orange-yellow precipitate with platinic chloride.

When ammonia is added to a solution of potassium osmate, the liquid assumes a wine-yellow colour; and, on addition of hydrochloric acid and subsequent neutralisation with ammonia, gives crystalline precipitates with ammonium oxalate, auric chloride, mercuric chloride, &c. It therefore contains a metallamine of some kind, possibly the osmium analogue of platinodiamine,  $\text{Pt}(\text{NH}_2)_2$ , or platino-ditetramine,  $\text{Pt}(\text{NH}_3)_4$ .

H. W.

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### Mineralogical Chemistry.

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**A curious Case of Isomorphous Admixture. Trichromates and Tetrachromates of Potassium and of Ammonium.** By G. WYROUBOFF (*Jahrb. f. Min.*, 1881, 2, Ref., 341—342).—Out of a warm nitric acid solution of 1 part potassium trichromate and  $1\frac{1}{2}$  parts ammonium trichromate, the author obtained, by slow cooling, three kinds of crystals. (1.) Small rhombic needles of the ordinary form of the ammonium salt. (2.) Monosymmetrical crystals of the ordinary form of the potassium salt. (3.) Large hexagonal crystals. Each of these contains both potassium and ammonium trichromate. According to generally accepted ideas, this would be explained by assuming that those two salts were trimorphous; but the author believes that this forms a new proof that bodies which are not isomorphous may crystallise together in variable proportions.

The tetrachromates of potassium and ammonium, which crystallise with difficulty, are most probably isomorphous and monosymmetrical.

H. B.

**The Geometrical Relations which exist between many Alkaline Chromates and also between many Alkaline Sulphates.** By G. WYROUBOFF (*Jahrb. f. Min.*, 1881, 2, Ref., 340—341).—Partly with the help of new observations, and partly using old data, the author discusses the forms of: potassium chromate (rhombic), potassium dichromate (asymm.), potassium trichromate (monosymm.), ammonium dichromate (monosymm.), ammonium trichromate (rhomb.). The primary forms of these may be so chosen that the relation of two of the axes of one of them is similar to the relation of the axes in the others. For these cases of external similarity of form, the author proposes to retain the name of Homöomorphism. This homöomorphism can occur between substances either chemically analogous or dissimilar. A number of compounds of the above chromates with other compounds are crystallographically and optically described.

In the second publication, two homöomorphous substances are described, viz., hexagonal potassium lithium sulphate, and rhombic ammonium lithium sulphate; this latter has a prism angle of  $119^{\circ} 57'$ , and its forms greatly resemble those of the hexagonal crystals. The mixed crystals are always biaxial, and are generally twins assuming a hexagonal symmetry; the axial angle varies. The author is of opinion that the hexagonal crystals of potassium sodium sulphate are not mixtures of non-isomorphous salts, but rather that two homöomorphous salts are present, viz., rhombic potassium sulphate ( $\infty P = 120^{\circ} 24'$ ), and a body,  $K_3Na(SO_4)_2$ , crystallising hexagonally. F. Klocke remarks that this salt has actually been described by Sénarmont. The author has also examined the two monosymmetrical bodies,  $3(NH_4)_2O, 4SO_3$  and  $3K_2O, 4SO_3$ , the last forming, however, trilling crystals.

H. B.

**The Minerals and Mineral Localities of North Carolina.**

By A. GENTH and W. C. KERR (*Jahrb. f. Min.*, 1881, 2, Ref., 338—339).—The authors, after speaking of former papers on the rarer minerals of this locality, give a complete list of 178 species, some of which have been found but quite recently.

H. B.

**Formula of Tetrahedrite.** By A. KENNGOTT (*Jahrb. f. Min.*, 1881, 2, Mem., 228—248).—The author discusses the recent analyses of H. Hidegh (*Jahrb. f. Min.*, 1880, vol. i, 334), which do not agree with the generally accepted formula,  $x(4R_2S, R_2S_3) + 4RS, R_2S_3$ ; three samples agreeing with  $2(4R_2S, R_2S_3) + 3RS, R_2S_3$ , and two others with  $3(4Cu_2S, R_2S_3) + 2(2RS, R_2S_3)$ , while a third sample from Szászka has the formula  $3Cu_2S, As_2S_3$ , and is accordingly not fahlerz, but julianite. This disagreement led the author to recalculate the results of all published analyses, numbering over ninety; of these, however, all those were excluded whose percentage of sulphur did not agree within  $\pm 1.50$  per cent. of that calculated on the components  $R_2S, R_2S_3$  and  $RS$ . A list of references of the available fifty-three analyses is given. These analyses were calculated to  $R_2S, R_2S_3$  and  $RS$ , and three tables are given in which the relationships between these substances are shown. After excluding from these tables ten analyses on account of various

reasons, it is shown that the remaining forty-three may be divided into three groups: (1) twenty-five agreeing with  $4R_2S, R_2S_3 + x(3RS, R_2S_3)$  where  $x$  varies from 0.390 to 1.030; (2) thirteen agreeing with  $4R_2S, R_2S_3 + x(4RS, R_2S_3)$ ,  $x$  varying from 0.358 to 0.985; and (3) five which agree with no particular formula. H. B.

**Occurrence of Realgar and Orpiment in Utah.** By W. P. BLAKE (*Jahrb. f. Min.*, 1881, 2, Ref., 340).—These two minerals occur side by side in a thin layer in dense, sandy clay, over which is a layer of lava. Antimony glance also occurs with them, as also does gypsum. The author believes that all these minerals penetrated into the already formed rocks. H. B.

**American Sulpho-selenides of Mercury, with Analyses of Onofrite from Utah.** By W. J. COMSTOCK (*Jahrb. f. Min.*, 1881, 2, Ref., 337—338).—The mineral was described by Newbury as selenide of mercury, but it has the composition—

Se.	S.	Hg.	Zn.	Mn.
4.58	11.68	81.93	0.54	0.69 = 99.42

Hence it is onofrite,  $Hg(SSe)$ , in which  $S : Se = 6 : 1$ . It forms a bed, 4 inches thick, in a palæozoic limestone. A list of all those sulphur and selenium compounds of mercury is given which occur only in North America. H. B.

**Boracite.** By H. PRECHT and B. WITTJEN (*Ber.*, 14, 2134—2138).—The samples of boracite from the carnallite beds are fine-grained to dense, have a conchoidal (frequently fragmentary) fracture, are of a white colour somewhat resembling dense limestone, but are mostly slightly greenish on account of small quantities of ferrous chloride; sp. gr. between 2.645 and 2.699. They absorb moisture from the air, owing to the presence of magnesium chloride, but may remain under water for some time in small lumps without falling to pieces. The samples of boracite from the kainite beds are soft and pliant, have an uneven earthy fracture, and are yellow to reddish in colour on account of ferric oxide; sp. gr. between 2.542 and 2.573; under water they fall in pieces, making a slimy mass. Both varieties were well treated with water and analysed.

		From Carnallite.	From Kainite.
Soluble in water.	Magnesium chloride ..	5.09 per cent.	4.72 per cent.
	Magnesium sulphate ..	—	1.69
	Sodium chloride.....	0.80	0.50
	Potassium chloride....	0.24	1.85
	Boric acid .....	0.11	0.73
	Magnesium oxide ....	0.04	0.31
	Water .....	7.01	11.27
	Insoluble boracite ....	86.65	78.92

The washed boracites were very fine powders, and, when analysed, gave—

	From Carnallite.	From Kainite.
Magnesium oxide . . . .	30.78 per cent.	31.04 per cent.
Chlorine . . . . .	8.59 „	8.59 „

both agreeing with the formula  $2(3\text{MgO}, 4\text{B}_2\text{O}_3), \text{MgCl}_2$ . They are, therefore, identical. The result of an experiment on the effect of heating boracite does not support the statement that this mineral breaks up into magnesia and boric acid. An attempt to make the mineral, by dissolving boric acid in a concentrated solution of magnesium chloride, was not successful, magnesium borate being the product.

D. A. L.

**Kieserite.** By H. PRECHT and B. WITTJEN (*Ber.*, **14**, 2131—2134).—An analysis of a very pure sample of this mineral from the Stassfurt carnallite deposits gave:—

$\text{MgSO}_4$ .	$\text{H}_2\text{O}$ .	$\text{NaCl}$ .	$\text{KCl}$ .	$\text{MgCl}_2$ .
86.062	13.320	0.344	0.156	0.118

The last two salts and part of the water owe their presence to the admixture of carnallite. Kieserite,  $\text{MgSO}_4 + \text{H}_2\text{O}$ , is broken up by water into a crystalline meal, which sets to a hard cement-like mass in the air. The authors show that this is not due to the binding power of the above chlorides as is generally supposed, but rather to the compression of the mineral itself. Kieserite is formed when a concentrated solution of magnesium sulphate is poured into a hot saturated solution of magnesium chloride.

Another sample of mineral taken from between the rock-salt and carnallite consisted of 66 per cent. sodium chloride and 34 per cent. kieserite. This kieserite has not the property of the above sample, for it can remain a long time in cold water without changing; it dissolves in hot water in 3—4 hours, but does not set like a cement.

D. A. L.

**Krugite.** By H. PRECHT (*Ber.*, **14**, 2138—2139).—This mineral is found in the rock-salt deposits in New-Stassfurt. It is somewhat similar to polyhalite, the chief difference being its constitution, which is  $\text{K}_2\text{SO}_4, \text{MgSO}_4, 4\text{CaSO}_4, 2\text{H}_2\text{O}$ , probably a mixture of anhydrite and polyhalite. Analysis gave—

	Found.		Calculated.
Potassium sulphate ..	18.60	17.85	19.90 per cent.
Magnesium sulphate .	13.71	13.34	13.74 „
Calcium sulphate ....	63.15	63.85	62.24 „
Water.....	4.16	4.20	4.12 „
Sodium chloride ....	0.38	0.80	—

It is crystalline; hardness 3.5; sp. gr. 2.801. A microscopic examination of thin plates with polarised light show it to be a chemical compound. With hot water it acts like polyhalite, potassium and magnesium sulphates being dissolved, the gypsum remaining behind. With cold water magnesium sulphate is dissolved, and the double salt  $\text{K}_2\text{SO}_4, \text{CaSO}_4 + \text{H}_2\text{O}$  is left insoluble.

D. A. L.

**The Vanadium Minerals from Cordoba State, Argentine Republic.** By C. RAMMELSBURG (*Jahrb. f. Min.*, 1881, 2, Ref., 330—331).—The first part of this paper agrees in general with that of a former paper (Abstr., 1881, p. 1000). Analyses are given by Döring, of Cordoba, of (1) Descloizite; (2) A new vanadate, Brackebuschite, which forms small black striated prisms:—

	Cl.	V <sub>2</sub> O <sub>5</sub> .	As <sub>2</sub> O <sub>5</sub> .	PbO.	ZnO.	MnO.	FeO.
I. (a)	0.43	20.78	0.23	56.89	16.52	—	2.57
(b)	0.08	22.59	0.27	56.00	17.02	0.40	0.26
(c)	0.27	21.85	0.30	56.01	17.56	0.77	0.07

	CuO.	H <sub>2</sub> O.	Insoluble.
I. (a)	0.42	—	0.03
(b)	0.02	2.14	0.31 = 99.09
(c)	0.40	2.57	0.78 = 100.58

	V <sub>2</sub> O <sub>5</sub> .	P <sub>2</sub> O <sub>5</sub> .	PbO.	MnO.	FeO.	ZnO.	CuO.	H <sub>2</sub> O.
II.	25.32	0.18	61.00	4.77	4.65	1.29	0.42	2.03 = 99.66

Hence it is  $R_3V_2O_8 + Aq.$

H. B.

**Schneebergite, a New Mineral.** By A. BREZINA (*Jahrb. f. Min.*, 1881, Ref., 331—332).—It occurs in gypsum and anhydrite, near their contact with copper pyrites and magnetic iron; locality Schneeberg in Tyrol. Transparent, honey-yellow imbedded octohedrons; lustre glassy to adamantine; brittle; H. = 6.5; sp. gr. = 4.1. They have the angles and optical characters of regular octohedrons; decomposed with great difficulty by fused sodium potassium carbonate. Qualitatively analysed, the mineral was found to consist essentially of antimony, lime, and iron, with traces of copper, bismuth, zinc, magnesium, and sulphuric acid. The crystals often contain enclosures of magnetic iron, and then in polarised light show a black cross, which further is sometimes surrounded by concentric circles. Such appearances have been shown by several observers, and recently by F. Klocke (*Jahrb. f. Min.*, 1881, Mem. 249), to be characteristic of double refraction caused by pressure.

H. B.

**Crystallised Danburite from Russel.** By G. J. BRUSH and E. S. DANA (*Jahrb. f. Min.*, 1881, 2, Ref., 334—337).—This mineral had previously only been known in very poor crystals, and was considered as asymmetrical. It has now been found massive and in the most beautiful crystals in a granite rock, in which they line the cavities and fissures, and are accompanied by bright-green pyroxene, brown tourmaline, mica, quartz, and iron pyrites; the cavities were formerly probably filled with calcite. The crystals vary from a microscopic size to  $4\frac{1}{2} \times 2\frac{1}{2}$  inches. H. = 7—7.25; sp. gr. 2.986—3.021. Faces lustrous. Colours yellow, brown, white, and sometimes perfectly transparent. The crystals have a prismatic type, and greatly resemble topaz. Crystalline system, rhombic with  $a : b : c = 1.0000 : 1.8367 : 0.8830$ . Observed forms  $0P \cdot \infty P \infty \cdot \infty P \infty \cdot \infty P \frac{3}{2} \cdot \infty P \cdot \infty P \frac{3}{2} \cdot \infty P \frac{2}{3} \cdot \infty P \frac{4}{3} \cdot \frac{1}{3} P \infty \cdot P \infty \cdot 3P \infty \cdot 2P \infty \cdot 4P \infty \cdot 8P \infty \cdot 16P \infty \cdot 3P \frac{3}{2} \cdot P \cdot 2P \cdot \frac{1}{2} P \frac{2}{3}$ .

P $\check{2}$ . 2P $\check{2}$ . 2P $\check{4}$ . 4P $\check{4}$ . The close agreement between the interfacial angles of danburite and topaz is very striking; the axial relations for topaz are  $\check{a} : \check{b} : \check{c} = 1.0000 : 1.8920 : 0.9024$ . The plane of the optical axes is OP, the acute bisectrix for red and yellow is the axis  $b$ , and is negative, but for blue and violet it is the axis  $a$ , and is positive. Sections parallel to  $\infty P \infty$  and  $\infty P \check{\infty}$  gave the following optical data:—2V (bisectrix  $b$ ) for Li =  $87^{\circ} 37'$ ; for Na =  $88^{\circ} 23'$ ; for blue light—an ammoniacal copper solution— $90^{\circ} 56'$ ; and  $\mu = 1.634$  Li, 1.637 Na, and 1.646 for blue light. The mean of two analyses gave:—

SiO <sub>2</sub> .	Bo <sub>2</sub> O <sub>3</sub> .	CuO.	Al <sub>2</sub> O <sub>3</sub> .	Loss on ignition.
48.23	26.93	23.24	0.47	0.63 = 99.50

Thus agreeing with the formula  $\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot 2\text{SiO}_2$  first given to danburite in 1853. H. B.

**Danburite from Danbury.** By A. DES CLOIZEAUX; **Danburite from Russel, St. Laurent Co., N.Y.; Triphane from North Carolina; Fergusonite from Burke Co., North Carolina.** By L. SMITH (*Jahrb. f. Min.*, 1881, 2, Mem. 337).—Des Cloizeaux, in bringing before the French Mineralogical Society the preceding account of danburite, stated that there had long been doubt as to the crystalline system, since the appearance of the optical axes was exactly that of a rhombic crystal; measurements of the axial angles are given which agree fairly with those above referred to. Specimens of danburite and triphane—"bright green pyroxene"—from this new locality were exhibited.

H. Smith described fergusonite from Burke Co. as showing distinctly the pyramidal hemihedrons, but being totally free from tantallic acid; it contains 48.12 per cent. niobic acid. H. B.

**A Blue Mineral from Chaponost (near Lyons) discovered by M. Gonnard; another Blue Mineral from Chili by E. BERTRAND; the Existence of a New Mineral Species, Dumortierite, in Gneiss, from Beaunan, near Lyons, by F. GONNARD; Analysis of Dumortierite.** By A. DAMOUR (*Jahrb. f. Min.*, 1881, 2, Ref., 329—330).—This mineral forms small elongated crystals on felspar, which are not capable of goniometrical measurements. The optical characters are those of a rhombic crystal; the axial angle is small and  $\rho < v$ ; they show a very marked pleochroism: with the length of the crystal parallel to the polarising plane of the nicol prism, they appear white, and when turned through a right angle they appear of a beautiful smalt-blue; the crystals are always twinned, the axial planes making an angle of nearly  $120^{\circ}$ . For analysis, the substance was isolated by treating with hydrofluoric and sulphuric acids, and by the use of Thoulet's solution. Sp. gr. = 3.36—3.37. On ignition it becomes colourless. The analysis gave—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO <sub>3</sub> .	MgO.	Loss on ignition.
29.85	66.02	1.01	0.45	2.25 = 99.58



The  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$ , give the formula  $4\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ . The blue mineral from Chili is not dumortierite, perhaps corundum.

H. B.

**Philadelphite, a New Mineral Species.** By H. C. LEWIS (*Jahrb. f. Min.*, 1881, 2, Ref., 339).—Pearly lustre; brown or yellow colour; the thin lamellæ are flexible but not elastic; tough; fatty feeling; monosymmetrical. Cleavage basal; sometimes also in two directions parallel and perpendicular to the plane of the optical axes. On heating, it increases in volume tenfold and swells with such force that 2.5 grams will lift ten pounds. Its analysis gave—

$\text{SiO}_2$ .	$\text{TiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{V}_2\text{O}_5$ .	$\text{FeO}$ .	$\text{MnO}$ .	$\text{NiO}, \text{CoO}$ .	$\text{CuO}$ .
35.73	1.03	15.77	19.46	0.37	2.18	0.50	0.06	0.08

$\text{MgO}$ .	$\text{CuO}$ .	$\text{Na}_2\text{O}$ .	$\text{Li}_2\text{O}$ .	$\text{K}_2\text{O}$ .	$\text{P}_2\text{O}_5$ .	$\text{Cl}$ .	$\text{H}_2\text{SO}_4$ .	$\text{H}_2\text{O}$ .
11.56	1.46	0.90	trace	6.18	0.11	trace	trace	4.34 = 100.45

Hence the formula  $\text{R}''_4\text{R}^{\text{vi}}_2\text{Si}_5\text{O}_{20}2\text{H}_2\text{O}$ .

H. B.

**Cossyrite, a New Mineral from Liparite Lavas of the Island Pantellaria.** By H. FÖRSTNER (*Jahrb. f. Min.*, 1881, 2, Ref., 332—334).—The small imbedded crystals of this body were formerly described by the author as common hornblende. The crystals are 1.5 mm. long, black, with a vitreous lustre on the prismatic faces, the others dull. Cleavage parallel to two prismatic faces, which make an angle of  $114^\circ 9'$ . Crystalline system, asymmetrical with the axial relations  $a:b:c = 0.6469:1:0.6635$ ;  $\alpha = 109^\circ 16'$ ;  $\beta = 107^\circ 52'$ ;  $\gamma = 84^\circ 30'$ ; observed forms  $\infty\text{P}'_1 \cdot \infty_1\text{P} \cdot 0\text{P} \cdot \text{P}_1 \cdot \infty\bar{\text{P}}\infty \cdot \infty\bar{\text{P}}\infty \cdot \infty\bar{\text{P}}'_3 \cdot \infty_1\bar{\text{P}}'_3 \cdot \frac{1}{3}_1\bar{\text{P}}_1\infty \cdot \frac{2}{3}_1\bar{\text{P}}_1\infty \cdot 2_1\bar{\text{P}}'_1\infty \cdot 2_1\bar{\text{P}}'_1\infty \cdot 4_1\bar{\text{P}}'_1\infty \cdot \frac{1}{2}\text{P}_1 \cdot \frac{1}{3}\text{P}_1 \cdot 3\bar{\text{P}}'_3 \cdot \frac{2}{3}\bar{\text{P}}'_3 \cdot \text{P} \cdot \frac{1}{2}_1\bar{\text{P}}'_1 \cdot \text{P}$ . Crystals, generally twins, twin plane  $\infty\text{P}\infty$ . The individual measurements often differ considerably, but the mean values agree with the above elements. The analysis afforded—

$\text{SiO}_2$ .	$\text{Fe}_2\text{O}_3$ .	$\text{Al}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{MnO}$ .	$\text{CuO}$ .	$\text{CaO}$ .
43.55	7.97	4.96	32.87	1.98	0.39	2.01

$\text{MgO}$ .	$\text{Na}_2\text{O}$ .	$\text{K}_2\text{O}$ .
0.86	5.29	0.33 = 100.21

Sp. gr. = 3.74—3.75. Sections are transparent at the edges only; they show numerous internal fractures and brown transparent enclosures; the depolarising directions in sections parallel to  $\infty\text{P}\infty$  and  $\infty\bar{\text{P}}\infty$  are inclined  $3^\circ$  and  $39^\circ$  respectively to the vertical axis.

H. B.

**The Basalts of Sicily.** By L. RICCIARDI and S. SPECIALE (*Gazzetta*, 1881, 359—392).—This paper contains descriptions and analyses of numerous Sicilian basalts from the Scogli dei Ciclopi, Aci-Castello, Malta, Diagio, Paterno, Sentini, Palagonia, Militello, and Pachino. The general conclusions drawn from these analyses are as follows:—

1. The basalts of Sicily are all hydrated, the amount of water of hydration varying in the undecomposed basalts from 0.72 to 9.26 per cent., and increasing in the decomposed basalts to 3.82—19.08 per cent.

2. The basalts by their decomposition yield a plastic argillaceous fertile soil, the fertility of which is due to the large proportion of phosphoric acid and alkalis occurring in the rocks.

3. The decomposed basalts differ from the undecomposed rocks in containing a larger proportion of silica, excepting that of Aci-Castello, in which the proportion of silica is less than that which is present in the undecomposed rock, an exception which may perhaps be due to the large quantity of zeolites contained in the undecomposed rock.

4. The quantities of phosphoric acid and lime diminish in the decomposed rock; also the magnesia and alkalis, but chiefly the potash.

5. The sesquioxides of iron and aluminium increase in the decomposed basalts; the ferrous oxide on the other hand diminishes perceptibly in some of these decomposed rocks, and in others disappears completely.

H. W.

**Orientation of the Cleavage Planes in Iron Meteorites by means of Widmannstadt's Figures.** (*Chem. Centr.*, 1881, 386.)

**Meteoric Iron from Lexington Co., S. Carolina.** By C. U. SHEPARD (*Jahrb. f. Min.*, 1881, 2, Ref., 343).—This mass of 10½ pounds, found in 1880, contains numerous cavities filled with troilite. The section shows the peculiar lustre, called metallic moirée. Iron nickel phosphide is contained in clefts and cavities. For analysis portions were taken as free from troilite as possible.

Fe, with trace of Mn.	Ni.	Co.	Insoluble, with traces of Sn and P.	
92.416	0.077	0.927	0.264	= 99.684
H. B.				

**Meteoric Iron from Whitfield Co., Georgia.** By W. E. HIDDEN (*Jahrb. f. Min.*, 1881, 2, Ref., 343).—This mass weighing 13 lbs., found in 1877, contains much chloride of iron. Brezina had already brought this meteorite before the Vienna Academy (see below).

H. B.

**Preliminary Notice of New or but little known Meteorites.** By A. BREZINA (*Jahrb. f. Min.*, 1881, 2, Ref., 342—343).—Five specimens are from the United States, viz.: (1.) Butler, Bates Co., Missouri, known since 1875. (2.) Tazewell, Claiborne Co., Tennessee, 1853. (3.) Casey Co., Georgia, 1877. (4.) Whitfield Co., Georgia, 1878. (5.) De Calb Co., Caryfort, Tennessee, 1840. All these are iron meteorites, and show a more or less prominent crystalline structure; they mostly contain also troilite, schreibersite, and No. 4 contains veins filled with magnetic iron ore. A specimen from Kalumbi, Presidency of Bombay, and which fell Nov. 4, 1879, has a light yellow colour, and contains particles of oxidised iron. Further examination is promised.

H. B.

## Organic Chemistry.

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**Tertiary Butyl Bromide.** By H. W. ROOZEBOOM (*Ber.*, **14**, 2396—2398).—Tertiary butyl bromide, prepared by passing a slow stream of isobutylene through hydrobromic acid, boils at 72°, and has the sp. gr. 1.215 at 20°. W. C. W.

**Trimethylene.** By A. FREUND (*Monatsh. Chem.*, **2**, 642).—Trimethylene bromide is strongly attacked by sodium at temperatures near its boiling point and under ordinary pressure, a regular stream of gas being evolved, consisting of trimethylene,  $\text{CH}_2\text{CH}_2\text{CH}_2$ , isomeric with ordinary propylene. Bromine absorbs it, but much less readily than the latter, reproducing the bromide. It unites with hydrogen iodide, forming normal propyl iodide,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ . H. W.

**Silicopropyl Compounds.** By C. PAPE (*Ber.*, **14**, 1872—1876).—By heating zinc propyl with silicochloroform in sealed tubes at 150° a mixture of *silicodecane* and *silicotetrapropyl* is obtained thus:— $2\text{SiHCl}_3 + 3\text{Zn}(\text{C}_3\text{H}_7)_2 = 2\text{SiH}(\text{C}_3\text{H}_7)_3 + 3\text{ZnCl}_2$  and  $2\text{SiHCl}_3 + 4\text{Zn}(\text{C}_3\text{H}_7)_2 = \text{SiH}(\text{C}_3\text{H}_7)_3 + \text{Si}(\text{C}_3\text{H}_7)_4 + 3\text{ZnCl}_2 + \text{Zn} + \text{C}_3\text{H}_8$ ; these two compounds may be separated by fractional distillation. The former is a colourless liquid (b. p. 170°, sp. gr. 7.923), insoluble in water, soluble in alcohol and ether; it burns with a bright flame with separation of silica. By the action of bromine, bromosilicodecane is obtained as a golden fuming liquid (b. p. 213°), converted by ammonia in aqueous solution into the corresponding silicotripropyl alcohol,  $\text{SiOHPr}_3$  (b. p. 205—208°) and by dry silver acetate into silicotripropyl acetate (b. p. 212—216°). Silicotetrapropyl is a colourless liquid (b. p. 213°, sp. gr. 7.979), insoluble in water and concentrated sulphuric acid, soluble in alcohol and ether. V. H. V.

**Double Cyanides of Metals of the Iron Group.** By A. DESCAMPS (*Ann. Chim. Phys.* [5], **24**, 178—199).—The action of alkaline cyanides on metallic cyanides proceeds in two distinct directions. In one case a double cyanide with potassium cyanide is formed, as in the case of zinc, nickel, and silver. On the other hand, bodies resembling ferro- and ferri-cyanides are obtained.

*Potassium Manganocyanide.*—This body is obtained by treating a concentrated solution of potassium cyanide, heated to 40° or 50° with either manganese dioxide or manganese carbonate, or better, freshly precipitated manganese cyanide. The salt forms dark violet plates. It changes rapidly in the air, absorbing oxygen, and decomposing into manganicyanide and manganese sesquioxide. It can be kept in a concentrated solution of potassium cyanide or in alcohol. It is decomposed by heat. On treatment with water it dissolves rapidly, yielding a green precipitate, which appears to be a manganocyanide

of manganese and potassium, corresponding to the ferrocyanide of iron and potassium, obtained by the action of dilute sulphuric acid on potassium ferrocyanide. When a solution of potassium cyanide is poured into manganese chloride, a reddish-white precipitate of manganese cyanide is obtained. In presence of a slight excess of potassium cyanide, however, this precipitate becomes green. After dissolving it in potassium cyanide and heating to  $50^{\circ}$ , large crystals of potassium manganocyanide separate out on cooling.

*Manganocyanic acid* is obtained by the action of hydrogen sulphide on lead manganocyanide suspended in water, and separates in small groups of colourless crystals on evaporating the filtrate in a vacuum. The compound rapidly undergoes decomposition in the air.

*Potassium manganocyanide with potassium ferrocyanide.*—This double salt has been obtained by treating manganese ferrocyanide with a concentrated solution of potassium cyanide at  $60^{\circ}$ ; on cooling, the double salt is deposited in greenish crystalline scales, which are soluble in water, but readily decompose in the solution.

*Potassium manganocyanide with potassium chloride* is obtained by allowing a solution of potassium manganocyanide in potassium cyanide to crystallise with potassium chloride. It forms small blue crystals, which are changeable in air. They are soluble in water, but insoluble in alcohol. Their solution rapidly decomposes. *Sodium manganocyanide* forms dark-blue crystals, which are soluble in water, but insoluble in alcohol. Its properties are almost identical with those of the potassium salt. *Barium manganocyanide* is obtained by slightly heating manganese carbonate, oxide, or cyanide with a concentrated solution of barium cyanide, and evaporating the filtrate in a vacuum. The crystals thus obtained are washed with alcohol and kept under alcohol; they have a dark-blue translucent appearance, and are soluble in water. They undergo decomposition in the air, and on treatment with water. The green compound formed in the decomposition can also be obtained by precipitating a salt of manganese with a concentrated solution of barium cyanide. *Barium potassium manganocyanide* is obtained by dissolving the above green precipitate in potassium cyanide. It is also formed when potassium manganese manganocyanide is dissolved in barium cyanide. It crystallises in small bluish crystals. *Strontium manganocyanide* in mode of preparation and properties resembles the barium salt, as does also the *calcium* salt. Manganocyanides give with metallic salts, precipitates which have the following colours:—Zn, violet; Cd, violet; Al, violet; Mn, green; Co, brownish-red; Pb, yellow; Cu, brownish-red.

Manganicyanides are converted into manganocyanides when treated with sodium-amalgam.

*Potassium Cobaltocyanide.*—When a concentrated aqueous solution of potassium cyanide cooled to  $0^{\circ}$  is added gradually to a cold solution of cobalt trichloride a reddish precipitate changing to green is obtained. It consists of cobalt potassium cobaltocyanide. On adding it to a concentrated solution of potassium, barium, or calcium cyanide, the corresponding cobaltocyanide is obtained. On addition of alcohol it deposits amethyst violet-coloured crystals. Alkaline cobalto-

cyanides give with metallic salts the following reactions:— $\text{ZnSO}_4$ , red precipitate insoluble in excess of reagent;  $\text{Al}_2(\text{SO}_4)_3$ , red gelatinous precipitate;  $\text{CdSO}_4$ , rose;  $\text{AgNO}_3$ , rose;  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , yellow;  $\text{HgCl}_2$ , orange. *Barium cobaltocyanide*, obtained from cobalt chloride and barium cyanide, resembles the potassium salt.

Anhydrous cobaltocyanic acid is colourless, and rapidly decomposes in the air. *Strontium cobaltocyanide* is prepared like the barium salt. It forms with potassium ferrocyanide a double salt, which can be obtained in well-formed green crystals.

*Chromocyanides*.—These compounds are very unstable, and require a very low temperature for their formation. When chrome-alum is reduced with zinc and precipitated with sodium acetate, a red compound is obtained, which can be washed with water containing carbonic anhydride. This salt is then gradually added to a cold concentrated solution of potassium cyanide, and on adding alcohol, a blue crystalline precipitate resembling potassium manganocyanide is obtained. An intermediate green compound exists. Chromocyanides give the following reactions with metallic salts:— $\text{BaCl}_2$ , reddish precipitate;  $\text{ZnCl}_2$ , reddish unstable precipitate;  $\text{PbO}$ , yellow;  $\text{HgO}$ , greenish-blue;  $\text{FeO}$ , red.

The author has obtained a series of bodies analogous to the nitroprussides.  
J. I. W.

**Formation and Preparation of Trimethylene Alcohol from Glycerol.** By A. FREUND (*Monatsh. Chem.*, **2**, 636—641).—In attempting to prepare normal butyl alcohol by the schizomycetic fermentation of glycerol, according to Fitz's method (this Journal, 1877, **2**, 214) the author observed that the once fermented liquid, in spite of the presence of apparently unaltered glycerol, could no longer be made to ferment, even after the butyl alcohol resulting from the first fermentation had been distilled off; and further examination showed that this residue contained neither glycerol nor any compound isomeric therewith: for on distilling it with superheated steam and redistilling the distillate thus obtained, the greater part passed over without decomposition between  $210^\circ$  and  $220^\circ$ . By repeated distillation a liquid was obtained which boiled constantly at  $216\text{--}216.5^\circ$  (thermometer wholly in the vapour) under a pressure of 736 mm. This boiling point and the other properties of the liquid show that it consists of trimethylene alcohol or normal propylene glycol,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , a conclusion confirmed by its analysis and by the properties of the halogen derivatives prepared from it. Its specific gravity was found to be 1.0536 at  $18^\circ$  compared with water at  $4^\circ$ . According to Reboul, who discovered this glycol (*Compt. rend.*, **79**, 169), its sp. gr. is 1.053 at  $19^\circ$ , and its corrected boiling point  $216^\circ$ .

*Trimethylene chloride*,  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ , was prepared by saturating the alcohol with hydrogen chloride, adding a double volume of fuming hydrochloric acid, and heating the liquid in sealed tubes for some hours in a water-bath. When freed from unaltered alcohol and the corresponding chlorhydrin by agitation with fuming hydrochloric acid, and further purified by washing with water, drying, and distillation, it forms a mobile, colourless, fragrant liquid, boiling under

pressure of 740 mm. at  $119.5^{\circ}$ , and having a density of 1.8996 at  $17.6^{\circ}$  (water at  $4^{\circ} = 1$ ).

The *bromide*,  $\text{CH}_2\text{Br}.\text{CH}_2.\text{CH}_2\text{Br}$ , prepared like the chloride, is a colourless, heavy but mobile, strongly refracting liquid, of peculiar odour, boiling at  $164.5$ — $165.5^{\circ}$  under a pressure of 731 mm., and having a density of 1.9228 at  $17.6^{\circ}$  (water at  $4^{\circ} = 1$ ). According to Geromont (*Ber.*, **4**, 549), it has a sp. gr. of 2.0177 at  $0^{\circ}$ , and boils at  $160$ — $163^{\circ}$  (bar. 719 mm.).

The *iodide*,  $\text{CH}_2\text{I}.\text{CH}_2.\text{CH}_2\text{I}$ , not hitherto known, is prepared like the bromide. It is a heavy liquid boiling with decomposition at about  $227^{\circ}$ , and having a density of 2.5631 at  $19^{\circ}$  compared with water at  $4^{\circ}$ . Its odour resembles that of the bromide, but is fainter.

The formation of trimethylene alcohol in the schizomycetic fermentation of glycerol takes place by abstraction of oxygen from the  $\text{CH}.\text{OH}$  group of the latter:  $\text{CH}_2(\text{OH}).\text{CH}(\text{OH}).\text{CH}_2.\text{OH} - \text{O} = \text{CH}_2(\text{OH}).\text{CH}_2.\text{CH}_2.\text{OH}$ ; but whether this oxygen is abstracted by the hydrogen evolved in the fermentation, or is employed in the formation of the accompanying fatty acid, or is respired by the schizomycetes, cannot at present be determined. It is, however, interesting to observe that whereas purely chemical agents, such as hydriodic acid or sodium-amalgam, abstract either the whole of the oxygen of the glycerol, or only that which is attached to the external carbon-atoms, this vital deoxidation takes place by removal of oxygen from the middle carbon-atom.

The yield of trimethylene alcohol usually varies between 10 and 20 per cent. of the glycerol employed; sometimes, however, it is as much as 27 per cent. This glycol is therefore the chief product of the fermentation.

H. W.

**Oxidation of Mannitol by an Alkaline Solution of Potassium Permanganate.** By O. HECHT and F. IWIG (*Ber.*, **14**, 1760—1765).—According to Pabst (*Compt. rend.*, **91**, 728), the oxidation of mannitol by an alkaline solution of potassium permanganate yields a tribasic acid, which he terms dihydroxycitric acid, and infers from this that the constitutional formula of mannitol is not the one generally accepted. The authors have repeated these experiments, and have obtained the following products of oxidation: formic acid, oxalic acid, and a small quantity of tartaric acid. Further, a glucose is formed, which reduces Fehling's solution, and probably consists of manitose. The authors, therefore, conclude that these products of oxidation are quite in accordance with the generally accepted views as to the constitution of mannitol.

P. P. B.

**The Sugar of Oak-bark Tannin.** By C. BÖTTINGER (*Ber.*, **14**, 2390—2391).—A reply to Etti's remarks (*Ber.*, **14**, 1826) on the author's previous paper (*ibid.*, 1559).

W. C. W.

**Anhydrous Milk-sugar.** By M. SCHMOEGER (*Ber.*, **14**, 2121—2126).—When a solution of milk-sugar is evaporated alone over a briskly boiling water-bath, the sugar remains behind in an anhydrous state; a solution of this dry sugar prepared in the cold turns the plane of

polarisation at first only slightly (half rotation), but after some hours it increases in activity until the constant normal degree for milk-sugar is attained; ordinary milk-sugar, on the other hand, behaves in the opposite way, turning the plane very strongly at first (birotation), and then decreasing to the constant. If, however, the milk-sugar solution is evaporated with a water absorbing substance (dry sand, potassium carbonate, &c.), the solution of the dry sugar which remains behind shows slight birotation; the residue from milk treated similarly behaves in the same manner, hence the residual sugar is anhydrous. Some milk-sugar solution evaporated over a water-bath on a mica plate, was left as a crystalline dry sugar, very soluble in water but not hygroscopic; the solution was slightly birotatory. Another experiment tried with milk-sugar and milk pointed to the fact that the sugar was left in the anhydrous condition after evaporation.

D. A. L.

**Levulose.** By JUNGLEISCH and LEFRANC (*Compt. rend.*, **93**, 547—550).—The authors state that it is incorrect to call levulose non-crystallisable sugar, for they show that when pure it can be obtained in a crystalline form. One of the best methods of obtaining it in a state of purity, is that of preparing it from inulin. The inulin is dissolved in 10 times its weight of water, and heated at about 100° for 20 hours: the solution is then evaporated to a syrup, and purified by treatment with alcohol and animal charcoal. The levulose has a great affinity for water, and will not crystallise on simple evaporation. In order to obtain it crystalline, the concentrated syrup is treated repeatedly with absolute alcohol, which removes all the water, and the remaining syrup is then sealed up in a flask and left in a cold place; after a short time fine needles resembling crystals of mannitol begin to form. If the same residue is dissolved in warm absolute alcohol, and the mother-liquor which separates on cooling is removed before the ordinary temperature is reached, it yields the same crystals. The authors have also prepared levulose by heating inulin with sulphuric acid, but find that the crystals thus obtained are always mixed with bye-products. They have also prepared levulose from inverted cane-sugar. It was extracted as calcium levulosate, then treated with oxalic acid, and afterwards with powdered calcium carbonate and filtered. The filtrate yields crystalline levulose on treatment with absolute alcohol. The authors state that it is impossible to perceive any difference between the two samples of levulose obtained from the preceding processes. A crystal of either of them destroys supersaturation in solutions of the other. Levulose crystallises in spherical groups of fine colourless crystals often 0.01 meter in length. It melts at 95°. The rotatory power varies rapidly with the temperature and strength of the solution.

J. I. W.

**Levulin in Oak-bark.** By C. ETTI (*Ber.*, **14**, 1826—1828).—By shaking the alcoholic extract of oak-bark first with ether, then with ethyl acetate, evaporating the residue to dryness and exhausting it with water, the author obtained a solution containing tannin; after removing this by lead carbonate, the solution was found to contain

quercite and levulin, also a small quantity of a glucose and a small quantity of a red colouring matter. The quercite is separated from the levulin by precipitation with lead acetate. The author considers that the occurrence of levulose in oak-bark extract explains the fact that many observers have obtained sugar from tannin prepared from oak-bark extract, inasmuch as the precipitate of this substance with lead acetate retains the levulose, and is only with difficulty washed free from levulin. The author considers the method used by Böttinger (Abstr., 1881, 1022) to separate quercite and cane-sugar as ineffective for complete separation, especially in presence of levulin and levulose.

P. P. B.

**A New Carbohydrate.** By E. MORELLI (*Compt. rend.*, **93**, 646).—In 1850 Ganean extracted from Siberian saxifrage (*Bergenia Siberica*) a crystallisable substance, which he called bergenin. The author of the present memoir has submitted it to a close examination, and on account of its resemblance to mannitol, he proposes to call it *bergenitol*. It forms small, colourless, orthorhombic crystals, which have a bitter taste. It is laevorotatory  $[\alpha]_D = -51^\circ 36'$ . It is very slightly soluble in cold alcohol and in water, the solubility increasing with the temperature. Its specific gravity is 1.5445. It melts at  $130^\circ$ . When heated with acetic acid in a sealed tube it yields a white amorphous acetyl compound, which is very soluble in water, alcohol, and ether. Its formula is  $C_8H_9O_5\text{Ac}$ . On heating for 24 hours at  $100^\circ$  with dilute sulphuric acid it yields bergenitole and acetic acid. The author has prepared a corresponding compound of valeric acid.

Acetic chloride dissolves bergenitol, and yields  $C_8H_7O_5\text{Ac}$ . Benzoic chloride yields a similar compound. On heating the acetyl compound in a sealed tube with acetic anhydride,  $C_8H_5O_5\text{Ac}_2$  is obtained. The carbohydrate is therefore a pentatomic alcohol, and is to be classed with pinitol and quercitol.

J. I. W.

**On a Nitric Ether formed by the Action of Nitric Acid on Glycogen.** By S. LUSTGARTEN (*Monatsh. Chem.*, **2**, 626—635).—This compound, designated by the author as *nitroglycogen*, is prepared by drenching and intimately mixing glycogen in a basin cooled with ice, first with fuming nitric acid, and then with strong sulphuric acid, and so on alternately, till altogether  $4\frac{1}{2}$  pts. nitric acid and  $10\frac{1}{2}$  pts. sulphuric acid have been used for 1 pt. of glycogen. During the treatment with nitric acid, part of the glycogen dissolves, the rest becoming translucent with yellowish colour, and on mixing with sulphuric acid, the nitroglycogen separates out in white nodular, glutinous lumps. The entire mass is then transferred to a large beaker, quickly mixed with a large quantity of water, several times decanted, then washed on the filter with distilled water till the reaction of sulphuric acid is no longer perceptible, and finally dried over sulphuric acid in the dark. The yield of the nitro-compound amounts to about 140 per cent. of the glycogen employed.

Nitroglycogen thus prepared forms partly white nodular lumps, partly a fine white powder. It is insoluble in water, ether, and alcohol, in hydrochloric and sulphuric acids, in ammonia, and in potash-ley,



the two latter colouring it yellow and brown on heating, and partly decomposing it. Ammonium sulphide and strong nitric acid dissolve and decompose it. No solvent for nitroglycogen has yet been found which does not at the same time decompose it. It is, moreover, decomposed, with formation of less highly nitrated compounds, by the action of daylight, and more quickly by exposure to direct sunshine; also by heating to 80—90°. When heated on platinum-foil it detonates, leaving a residue of charcoal, but it is not exploded by pressure or percussion. Its analysis leads to the formula  $C_6H_8N_2O_9 = C_6H_8(NO_2)_2O_5$ .

Nitroglycogen dissolves in ammonium sulphide, forming a clear, yellow-brown liquid; and on passing air through the solution till all the ammonium sulphide is removed, and the liquid is no longer alkaline, then evaporating to dryness on a water-bath, treating the residue with a small quantity of water, filtering off the separated sulphur, boiling the filtrate till the suspended sulphur cakes together, again filtering, and mixing the clear filtrate with four or five times its volume of absolute alcohol, a copious flocculent precipitate is obtained, which, when washed with absolute alcohol and dried over sulphuric acid, forms a loose white amorphous mass, and yields with water a clear, scentless, insipid solution, yellow and viscous in the concentrated state, and not coloured by iodine. These physical properties show that the substance in question is a dextrin, and this conclusion is confirmed by its chemical analysis, which leads to the formula  $C_6H_{10}O_5$ .

The specific rotatory power of this dextrin is  $[\alpha]_D = +194^\circ$ . Its reducing power is but small. By boiling with dilute sulphuric acid it is quickly and completely converted into dextrose; and the same change is quickly produced, at least in part, by the action of saliva. Like other dextrins it dialyses very slowly, so that a solution of it, after being subjected to dialysis for a week, exhibits but little decrease in its amount of dextrin. Alcohol added to its aqueous solution throws down, not a flocculent precipitate, but frequently an opalescent liquid, containing only a small quantity of pulverulent precipitate, or sometimes a turbid liquid, the turbidity of which is due to very fine particles, which show but little tendency to settle down, and quickly stop up the pores of a filter. A dialysed solution of ordinary dextrin obtained from starch was likewise not precipitated by alcohol, but merely became opalescent; but on adding to this dialysed solution small quantities of various salts—carbonates, sulphates, chlorides dissolved in water—or of potassium hydroxide in alcoholic solution, the addition of alcohol immediately produce a thick, flocculent precipitate, which quickly settled down, leaving the liquid quite clear. Dextrin thus prepared with non-volatile salts soluble in alcohol, retains 2 to 3 per cent. ash, even after prolonged washing, and that which is prepared with alcoholic potash retains even 5 to 6 per cent., so that in this latter case it is probable that a potassium-compound of dextrin is formed.

Commercial dextrin purified by dialysis and repeated precipitation with alcohol, is converted by the action of a mixture of nitric and sulphuric acids in the proportion above given for the treatment of glycogen, not into the nitroglycogen just described, but into a body probably identical with Béchamp's dinitrodextrin (*Compt. rend.*, **51**, 256). This

body forms a white amorphous mass, which is soluble in absolute alcohol, and decomposes readily with evolution of lower oxides of nitrogen. It likewise dissolves in ammonium sulphide, and when treated for nitroglycogen in the manner above described, yields a body having the characters of dextrin.

Nitroglycogen dissolves at ordinary temperatures in strong nitric acid, and water added to the solution throws down a dense white amorphous powder, which, after being well washed and dried over sulphuric acid, has the composition  $C_{12}H_{19}(NO_2)O_{10}$ . It is insoluble in water, alcohol, and ether, but dissolves in hydrochloric acid and in aqueous potash, both the acid and the alkaline solution yielding a white precipitate on neutralisation. This body likewise dissolves in ammonium sulphide, and when treated in the manner described for nitroglycogen, yields a dextrin-like body.

When nitroglycogen is heated with strong nitric acid, red fumes are evolved, and a solution is formed, which remains clear on dilution with water, and reduces Fehling's solution. Hence it appears that nitroglycogen is split up by hot nitric acid, the resulting dextrin being converted into glucose.

Nitroamylum prepared from starch also dissolves partially in ammonium sulphide, and the solution when treated as above described, likewise yields a dextrin-like body. H. W.

**Condensation-products of Isobutaldehyde.** By W. FOSSEK (*Monatsh. Chem.*, 2, 614—625).—The author has examined the products formed by heating isobutaldehyde with a strong solution of sodium acetate at  $150^\circ$ . After the heating had been continued for six or seven hours, the contents of the tubes were distilled with steam, whereupon there passed over, first a portion of the unaltered aldehyde, then a yellowish fragrant liquid, which dissolved in the layer of aldehyde. In the distillation-vessel there remained floating on the solution of sodium acetate, a somewhat viscid, yellow-brown liquid, having a faint but peculiar odour, together with a small quantity of a yellow resin.

The distillate separated into two layers, the upper of which was oily, and consisted mainly of unaltered isobutaldehyde, and a lower watery layer, from which, by a series of fractional distillations, for the details of which we must refer to the original paper, there was obtained a limpid, somewhat mobile liquid, distilling between  $149^\circ$  and  $151^\circ$ , having a fragrant etheric odour, and giving by analysis numbers leading to the formula  $C_8H_{14}O$ , which is that of a condensation-product of isobutaldehyde,  $2C_4H_8O - H_2O$ . This compound reduces an ammoniacal silver solution, with deposition of a silver speculum, and forms a crystalline compound with acid sodium sulphite. By oxidation with chromic acid mixture it is converted into acetic and isobutyric acid, and by slow oxidation in the air, into an unsaturated acid,  $C_8H_{14}O_2$ .

The high-boiling oil which partly goes over in the first distillation, as above mentioned, but remains for the most part in the retort, floating on the solution of sodium acetate, was purified by a series of distillations under reduced pressure, whereby it was obtained as a colourless, somewhat viscid liquid, having a faint but agreeable odour, and a harsh

bitter taste. It is insoluble in water, but dissolves readily in ether and in alcohol. It unites with hydrogen-sodium sulphite to a crystalline compound, and reduces ammoniacal silver nitrate, with specular deposition of silver. It is not altered by exposure to the air, and does not unite with bromine. Its analysis shows that it has the same percentage composition as isobutaldehyde, and from its vapour-density, for which the numbers 5.25 and 5.19 were obtained, it appears to be a polymeric modification of that compound,  $C_8H_{16}O_2$  (calc. vapour-density 5.00). By oxidation with chromic acid it is converted into isobutyric acid.

H. W.

**Action of Nitric Acid on Fatty Acids containing the Isopropyl Group.** By J. BREDT (*Ber.*, 14, 1780—1785). It has been already pointed out (*Annalen*, 208, 62) that the lactone of isocaproic acid, when oxidised by nitric acid, yields a monobasic acid, having the formula  $COOH.MeC<\overset{\overset{O}{\parallel}}{(CH_2)_2}>CO$ : this acid is not oxidised further

by nitric acid. The same acid is produced by the direct oxidation of isocaproic acid with nitric acid. The author has shown (*loc. cit.*) that this acid yields two series of salts, according as the neutralisation by alkaline carbonates takes place in cold or in hot solutions. The mono-silver salt has been obtained by neutralising the cold solution of the acid with silver carbonate, and removing the unaltered acid by means of ether. Of the lower homologues of isocaproic acid which contain the isopropyl group, isovaleric acid alone yields an acid similar to the above on oxidation, whilst isobutyric acid is either not acted on, or the products of oxidation are too unstable to be separated.

The action of nitric acid on isovaleric acid has been already studied by Desaignes (*Annalen*, 79, 374), who obtained a nitrovaleric acid, an indifferent body containing nitrogen, and a deliquescent acid; this last-named substance, the author has separated and purified; its formula is found to be  $C_6H_8O_6$ , and that of its calcium salt  $C_6H_6O_6Ca + 1\frac{1}{2}H_2O$ . The free acid is crystalline (m. p. 106°) and soluble in ether. It is probably identical with the methoxysuccinic acid obtained by Demarçay by the action of hydrocyanic acid on ethyl acetoacetate (*Compt. rend.*, 82, 1337), and described by Monis (this Journal, 1881, 376).

P. P. B.

**Di- and Tribromacrylic Acid.** By J. MAUTHNER and W. SUIDA (*Ber.*, 14, 1894—1895).—This paper is principally a discussion of the constitution of the dibromacrylic acid obtained from mucobromic acid.

V. H. V.

**Dissociation of Ammonium Carbonate.** By R. ENGEL and A. MOITESSIER (*Compt. rend.*, 93, 595—597).—The authors have previously shown that when two gaseous bodies on combining give a dissociable compound, the combination takes place only when the sum of the tensions of the components is greater than the tension of dissociation of the compound, whatever may be the tension possessed by each of the bodies. Accordingly, if a dissociable body is placed in presence of one of the substances produced by its dissociation, at a tension equal to or greater than the tension of dissociation at the temperature

of the experiment, or if a mixture in any proportion of the components is present (provided the sum of their tension is equal to the tension of dissociation), the dissociation of the body cannot take place. The authors find that ammonium carbonate exemplifies the law. The following are the results obtained :—

No. of experiment.	Volume.	Observed tension.	Tension of dissociation of carbonate.	Tension of CO <sub>2</sub> .	Tension of NH <sub>3</sub> .	Vol. at 0° and 160·1° deduced observed tension.	Temperature.
1	8·5	491·7	46·8	491·7	0	5·2	16·4
2	16·75	241·1	50·1	241·1	0	5·0	17·0
3	32·6	133·1	52·9	133·1	0	5·4	17·8
4	49·0	78·5	45·4	78·5	0	4·8	15·7
5	86·0	49·1	46·5	49·1	0	5·2	16·0
6	88·0	83·5	84·8	65·2	18·3	8·8	24·0
7	171·75	52·5	50·8	38·0	14·5	11·6	17·2
8	269·5	48·5	47·2	31·7	16·8	16·2	16·5
9	323·25	48·75	51·5	30·6	18·1	19·5	17·4

J. I. W.

**Action of Ammonia on Dibromosuccinic Acid and Ethyl Dibromosuccinate.** By T. LEHRFELD (*Ber.*, 14, 1816—1824).—*Diamidosuccinic acid*,  $[\text{CH}_2(\text{NH}_2)\text{COOH}]_2$ , is obtained by the action of ammonia on an alcoholic solution of dibromosuccinic acid in sealed tubes at 100°. It is insoluble in water, alcohol, and ether, but soluble in acids, alkalis, and alkaline carbonates. It does not form an ammonium salt, the free acid separating from its ammoniacal solution. The acid is a white powder, consisting of microscopic prisms, and when heated decomposes at 200°, without previously melting. It therefore differs entirely from the acid described by Claus and Helpenstein (*Abstr.*, 1881, 577). This acid is converted into tartaric acid by the action of nitrous acid. Besides this acid, other substances are formed by the action of ammonia on dibromosuccinic acid.

*Ethyl imidosuccinamate*,  $\text{NH} \begin{array}{l} \text{CH.CONH}_2 \\ | \\ \text{CH.COOEt} \end{array}$ , is obtained by the action

of ammonia on an alcoholic solution of ethyl dibromosuccinate at 60—80°. It crystallises in white needles, having a sweet taste and melting at 118°. It is soluble in the ordinary solvents, but insoluble in benzene and carbon bisulphide. It is very unstable, and its solutions decompose with formation of brown-coloured products. The properties of this substance are similar to those attributed by Claus and Helpenstein (*loc. cit.*) to ethyl diamidosuccinate.

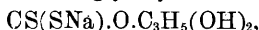
*Monethyl imidosuccinate*,  $\text{NH} \begin{array}{l} \text{CH.COOH} \\ | \\ \text{CH.COOEt} \end{array}$ , is obtained from the

corresponding succinamate by the action of hydrochloric acid. It crystallises from warm water in small needle-shaped crystals, having

a bitter taste (m.p.  $100^{\circ}$ ). It is a weak acid, but does not expel carbonic anhydride from carbonates. The potassium salt is obtained by adding the acid to alcoholic potash; the solutions of this salt produce precipitates with soluble calcium, silver, lead, mercuric, mercurous, and ferric salts. By the action of nitrous acid, monethyl imidosuccinate is converted into oxalic acid and a small quantity of a substance containing nitrogen.

P. P. B.

**Glyceryl Xanthates.** By W. F. LOEBISCH and A. LOOSS (*Monatsh. Chem.*, **2**, 372—381).—Sodium glyceryl xanthate,



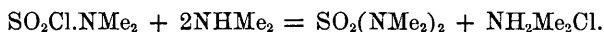
is obtained by heating sodium glycerate with excess of carbon bisulphate in closed vessels at  $55$ — $60^{\circ}$  for 24 hours. It then forms a deep red resinous mass, adhering strongly to the bottom of the vessel and melting under carbon bisulphide at  $30^{\circ}$ . It decomposes readily when heated in air; it is completely soluble in a little water, but the solution becomes turbid after a time. Addition of alcohol decolorises it, and a white precipitate is formed, insoluble in ether, chloroform, and benzene. Alkaline solutions of glyceryl xanthate remain unchanged for some days; acids cause, after a time, a precipitation of sulphur with liberation of carbon bisulphide; it was not found possible to isolate a glycerylxanthic acid. Lead acetate gives a purple-red precipitate with solutions of the sodium salt, soon turning brownish-red; silver nitrate gives a blackish-brown, and mercuric chloride a light yellow precipitate, all of which blacken in a few days. Addition of acetic acid and cupric sulphate causes a dark reddish-brown flocculent very voluminous precipitate of cuprous glycerylxanthate,  $\text{C}_6\text{H}_{14}\text{O}_6\text{Cu}_2\text{S}_4$ . If instead of the dried substance, sodium glycerate containing alcohol of crystallisation is employed in the preparation, the alcoholate



is obtained as a clear yellow viscous mass, similar in properties to the above, but still more unstable.

A. J. G.

**Action of Sulphuryl Chloride on Dimethylamine Hydrochloride.** By R. BEHREND (*Ber.*, **14**, 1810—1812).—*Dimethylamine sulphochloride*,  $\text{SO}_2\text{Cl.NMe}_2$ , is obtained by heating sulphuryl chloride with dimethylamine hydrochloride in a vessel connected with a reflux condenser. It is a colourless oil, heavier than water, and insoluble in water, acids, and alkalis (b. p.  $183$ — $187^{\circ}$ ). The accuracy of the above formula is confirmed by the fact that this compound forms tetramethylsulphamide (Abstr., 1881, 717), when treated with dimethylamine, thus:—



P. P. B.

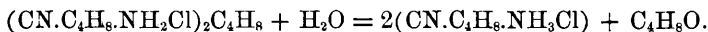
**Tri-isobutylidenediamine (a Hydramide of the Fatty Series).** By A. LIPP (*Ber.*, **14**, 1746—1750).—In a former communication (Abstr., 1881, 84) the author stated that when the compound of ammonia and isobutaldehyde (oxyheptaisobutylidenamine) is heated to  $145^{\circ}$ , it is resolved into ammonia, isobutaldehyde, and a base

$C_8H_{15}N$ . This reaction takes place in two phases: if oxyhepta-isobutylidenamine is distilled quickly, ammonia is evolved, and isobutaldehyde passes over, whilst the temperature rises to  $150^\circ$ ; the retort then contains an oily liquid, the composition of which is  $(C_4H_9)_3N_2$ . This decomposition is expressed as follows:— $C_{28}H_{62}N_6O = 2(C_4H_9)_3N_2 + 2NH_3 + C_4H_8O$ .

This compound,  $(C_4H_9)_3N_2$ , the author regards as a *hydramide*; it is decomposed by acids into isobutaldehyde and an ammonium salt, thus:  $(C_4H_9)_3N_2 + 3H_2O + 2HCl = 3C_4H_8O + 2NH_4Cl$ . Its constitution is, therefore, represented by the following formula:



It is insoluble in water, but imparts to it an alkaline reaction; alcohol and ether dissolve it easily. When heated quickly, it distils without decomposition, but if heated slowly it is decomposed. Alkalis have no action on it. Hydrocyanic acid converts it into a di-imido-nitrile, analogous to those described by Erlenmeyer and Schäuffelen (*Ber.*, **11**, 149) and by Plöchl (this Journal, **40**, 820). This compound is very unstable; by passing hydrochloric acid gas into its ethereal solution, a hydrochloride is obtained which is insoluble in ether, but soluble in alcohol. This salt is decomposed by water into the hydrochloride of amidisovaleronitril and isobutaldehyde, as follows:

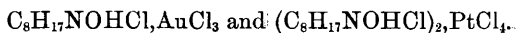


*Tri-isobutylenediamine*  $(C_4H_9)_3N_2$ , when heated at  $140$ – $145^\circ$ , is resolved into ammonia, the base  $C_8H_{15}N$ , and a viscous liquid. The base distils over at  $145$ – $147^\circ$ . It is a colourless strongly refractive liquid (b. p.  $145$ – $147^\circ$ ). It is insoluble in water, but imparts an alkaline reaction to the same; alcohol and ether dissolve it easily. Alkalis have no action on it, whereas acids decompose it with formation of isobutaldehyde and an ammonium salt. The existence in it of two carbon-atoms united by a double linking, is shown by the fact that it unites directly with bromine to form a dibromide,  $C_8H_{15}Br_2N$ , which forms prismatic crystals; it is very hygroscopic, and is decomposed by water.

Both the base  $C_8H_{15}N$  and the hydramide, when heated in sealed tubes at  $250$ – $270^\circ$ , yield a resinous mass, an oily base, and a gas burning with a luminous flame. The hydrochloride of the base forms deliquescent leaflets.

P. P. B.

**Alkines.** By A. LADENBURG (*Ber.*, **14**, 2406–2409).—*Piperpropylalkine*,  $C_8H_{17}NO$ , dissolves in water with evolution of heat. A portion of the base is reprecipitated from a concentrated aqueous solution by the addition of a little hydrochloric acid. The hydrochloride forms crystalline double salts with gold and platinum chlorides,



*Diethylpropylalkine*,  $C_7H_{17}NO$ , prepared from diethylamine and propylene chlorhydrin, boils at  $159^\circ$ . The platinochloride is freely soluble in water.

*Dimethylpropylalkine*,  $C_5H_{13}NO$  (b. p.  $125^\circ$ ), forms a platinochloride, crystallising in prisms.

*Dimethylethylalkine* (b. p. 130—134°) is prepared by the action of ethylene chlorhydrin on an aqueous solution of dimethylamine. On the addition of gold chloride to a concentrated solution of the hydrochloride, silky needles of the double salt,  $C_4H_{11}NOHCl, AuCl_3$ , are precipitated. The platinochloride is freely soluble.

*Conylethylalkine*,  $C_{10}H_{21}NO$ , boils at 241°.

W. C. W.

**Dipropylketine.** By P. P. TREADWELL (*Ber.*, **14**, 2158—2161).—A continuation of the author's researches on the ketines (Abstr., 1881, 895). Diethylketine combines readily with silver nitrate to form a crystalline compound of the formula  $C_{10}H_{16}N_3, AgNO_3$ , insoluble in water, sparingly soluble in dilute nitric acid. On boiling it for some time with water, it is decomposed into diethylketine, which passes over with the steam, while the silver nitrate remains in solution.

*Dipropylketine* is obtained by the reduction of nitrosopropylacetone, prepared by the process of V. Meyer and Züblin; on purification and fractional distillation of the crude product of the reaction, dipropylketine is obtained as a narcotic oil (b. p. 235—240°). This compound, unlike its homologues, is a monacid base, forming a platinochloride, of composition  $(C_{12}H_{20}N_2.HCl)_2PtCl_4$ . With silver nitrate, dipropylketine forms a sparingly soluble crystalline compound, which rapidly darkens on exposure to light, and is decomposed on boiling with water. Dipropylketine forms a characteristic bromo-derivative, which, in its properties, resembles the corresponding bromo-derivative of diethylketine.

V. H. V.

**Glyoxaline.** By H. GOLDSCHMIDT (*Ber.*, **14**, 1844—1848).—The author at the outset draws attention to the researches of Wyss on glyoxaline, and to the formula proposed to express the constitution of this compound (this Journal, 1878, 23). Following out the lines of Hofmann's experiments on piperidine and coniine (Abstr., 1881, 571, 746), the author has distilled in the dry way the methiodide of methylglyoxaline hydroxide, and has thereby obtained a base,  $C_4H_6N_2$ , as a dark oily liquid (b. p. 125°, sp. gr. 1.0359), soluble in water and alcohol. Its platinochloride crystallises in orange-red needles, insoluble in alcohol. It appears that this base resembles, in all its physical properties, the oxalmethylene of Wallach (Abstr., 1881, 572); but further examination is desirable. The question is also investigated whether the base obtained by the author is identical with methylglyoxaline obtained directly from methyl iodide and glyoxaline; but determinations of the solubilities of their platinochlorides proved that the two bases in question were isomeric. The dry distillation of the methhydroxide of the new base led to no result, and therefore the hydroxides of the glyoxaline derivatives do not, like other ammonium bases, lose nitrogen in the process.

V. H. V.

**Derivatives and Constitution of Thiocarbamide.** By B. RATHKE (*Ber.*, **14**, 1774—1780).—*Ethylthiocarbamilide*,  $C_{15}H_{16}N_2S$ , which has been already described by Will (Abstr., 1881, 906), is conveniently obtained as a hydrobromide by the action of ethyl bromide on thiocarbamilide. By boiling the product of this reaction with a solution of sodium carbonate, the free base is obtained.

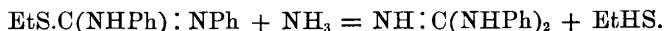
It crystallises in colourless needles, insoluble in water but soluble in alcohol; it melts at  $73^{\circ}$  (Will gives the m. p. as  $79^{\circ}$ ).

The *nitrate*, *sulphate*, *chloride*, *bromide*, and *iodide* of this base are described, they are formed by dissolving the base in the corresponding acid. These salts are soluble in water; the iodide is the least soluble, it crystallises with one mol. of  $\text{H}_2\text{O}$ . The iodide is unstable and easily decomposed into a polyiodide, which is formed as a brown crystalline precipitate when iodine is added to the solution of the iodide.

The *platinochloride*  $(\text{C}_{15}\text{H}_{16}\text{N}_2\text{S}, \text{HCl})_2\text{PtCl}_4 + 2\text{H}_2\text{O}$ , is obtained as a crystalline precipitate; it melts below  $100^{\circ}$ , and loses its water of crystallisation at  $100-110^{\circ}$ .

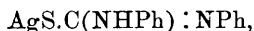
This base is only soluble in a large excess of acetic acid. With ammoniacal silver nitrate, its alcoholic solution gives a white precipitate, which is not blackened on heating: it gives no precipitate with lead acetate; if, however, potash is added to the warm solution, a precipitate of lead mercaptide is obtained, as ethylthiocarbanilide is decomposed by alcoholic potash, into diphenylcarbamide and potassium mercaptide.

This base is decomposed by alcoholic ammonia into mercaptan and diphenylguanidine, thus:



When chlorine or bromine acts on the aqueous solutions of ethylthiocarbanilide chloride or bromide, the group " $\text{C}_2\text{H}_5\text{S}$ " forms ethylsulphonic acid, and is replaced by an atom of chlorine or bromine. The chloro- and bromo-compounds are insoluble in water, but may be crystallised from alcohol or acetic acid; the constitution of these compounds is probably expressed by the formula  $\text{NHPh.CCl:NPh}$ .

The author considers that the constitution of thiocarbanilide is best expressed by the unsymmetrical formula  $\text{HS.C(NH}_2\text{):NH}$ , and thiocarbanilide by a similar formula. That thiocarbanilide yields silver sulphide when boiled with an acid or ammoniacal solution of a silver salt, is explained by the formation of a silver compound



which on heating gives silver sulphide. That ethylthiocarbanilide does not yield silver sulphide is explained by the fact that the hydrogen in the group HS is already replaced by the ethyl-group.

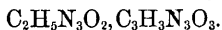
With an aqueous solution of thiocarbanilide, copper chloride gives a colourless crystalline precipitate, and this when suspended in water and treated with sulphuretted hydrogen, is decomposed, yielding copper sulphide, and a soluble compound containing copper, which is not precipitated by sulphuretted hydrogen. This compound forms colourless strongly refractive crystals,  $\text{CuClS.C(NH}_2\text{):NH}$ ; its solution when treated with copper chloride yields the original crystalline precipitate, which is probably a double compound of copper chloride with this compound.

P. P. B.

**Biuret Cyanurate.** By J. HERZIG (*Monatsh. Chem.*, **2**, 410—415).—In preparing a large quantity of biuret, a substance crystallised



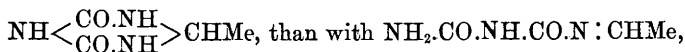
out first in anhydrous needles, and was supposed to be urea cyanurate; further examination proved it to be biuret cyanurate,



Baryta in the cold decomposed it into biuret and barium cyanurate; when it was treated with sodium hypobromite, the cyanuric acid group remained unchanged, whilst two-thirds of the nitrogen of the biuret group was set free.

A. J. G.

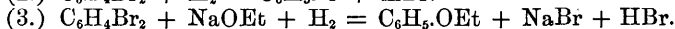
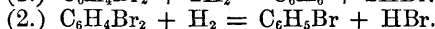
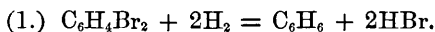
**Trigenic Acid.** By J. HERZIG (*Monatsh. Chem.*, 2, 398—409).—Trigenic acid, when heated with baryta-water in sealed tubes at 150—160°, yields nearly the whole of its nitrogen as ammonia, a slight odour of a pyridine base being noticed; no methylamine is formed. On dry distillation, it yields ammonia, ammonium carbonate, and a base, apparently collidine. Heated with methyl iodide and methyl alcohol in sealed tubes at 120—130°, trigenic acid yields carbonic anhydride, ammonium iodide, and in much smaller quantity, methyl-ammonium iodide; it was found that when urea and biuret were heated with these reagents, similar results were obtained. Trigenic acid when heated for six hours at 150° with hydrochloric acid, yields about two-thirds of its nitrogen as ammonium chloride: it is not decomposed by sodium hypobromite, and on oxidation with nitric acid gives carbonic anhydride, ammonia, and cyanuric acid. These results agree better with the formula



the formula previously suggested.

A. J. G.

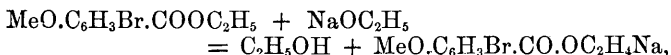
**Action of Sodium Ethylate on some Brominated Compounds of the Aromatic Group.** By L. BALBIANO (*Gazzetta*, 1881, 396—419).—1. Paradibromobenzene heated with sodium ethylate in sealed tubes for nine or ten hours, yields benzene, monobromobenzene, and phenetol. Now Merz and Weith have shown (*Ber.*, 1873, 1517) that sodium ethylate is resolved by heat into ethylene and sodium hydroxide, the latter then reacting with a fresh quantity of sodium ethylate, and converting it into sodium acetate, with evolution of hydrogen; and it is probable that a similar reaction takes place in the case under consideration, the liberated hydrogen giving rise to the compounds above mentioned in the manner shown by the following equations:—



The formation of the phenetol is perhaps, however, due to reduction of bromophenetol.

2. *Ethylie Bromanisate*,  $\text{MeO.C}_6\text{H}_3\text{Br.COOEt}$ , and *Sodium Ethylate*.—The reaction between these substances varies in character according to the temperature and the proportions in which they are mixed.

When the two substances are brought together in molecular proportions, at a slightly elevated temperature and under ordinary pressure, the sodium ethylate acts solely on the group  $\text{CO}_2\text{C}_2\text{H}_5$  of the bromanisic ether, according to the equation—



the action being in fact precisely analogous to that of sodium ethylate on the non-halogenated ethers of the fatty series.

At a somewhat higher temperature ( $180^\circ$ ) the principal reaction is still the same, but it is accompanied by another, which yields a new bromanisic acid, and a small quantity of a substance having the composition  $\text{C}_{40}\text{H}_{47}\text{BrO}_{23}$ , the formation of which appears, however, to depend on the presence of a slight excess of sodium ethylate.

At higher pressures and with 2 mols. sodium ethylate to 1 mol. ethyl bromanisate, the quantity of product resulting from the action of the sodium ethylate on the bromine becomes greater.

The new bromanisic acid,  $\text{MeO.C}_6\text{H}_3\text{Br.COOH}$ , above mentioned, crystallises from alcohol in small shining needles insoluble in cold, very slightly soluble in hot water, soluble in alcohol and ether, especially when warm, melting at  $211.5\text{--}212^\circ$  (corr.); ordinary bromanisic acid melts at  $218\text{--}218.5^\circ$  (corr.).

The *ethylic ether* of the new acid forms a white shining crystalline mass, which when dry begins to melt at  $53^\circ$ , and melts completely at  $59\text{--}60.5^\circ$  (ordinary bromanisic ether melts at  $73.5^\circ$  to  $74^\circ$ ). The *zinc salt* of the new acid crystallises in long slender shining prisms, having the composition  $(\text{C}_8\text{H}_5\text{BrO}_3)_2\text{Zn} + 4\text{H}_2\text{O}$ , and giving off their water at  $160\text{--}170^\circ$ ; that of the ordinary acid contains  $3\text{H}_2\text{O}$ , and does not undergo any physical change at  $180\text{--}190^\circ$ .

The relative positions of the radicles  $\text{MeO}$ ,  $\text{Br}$ , and  $\text{COOH}$ , in a monobromanisic acid may be either 1:2:4 or 1:3:4; but which of these two formulæ belongs to the old and which to the new modification, is a question which cannot be determined by the facts at present known.

H. W.

**Action of Bromine on Benzyl Cyanide.** By C. L. REIMER (*Ber.*, 14, 1797—1802).—In a former communication, the author has shown that stilbene dicyanide is obtained by the action of bromine on benzyl cyanide at  $160\text{--}180^\circ$  (*Ber.*, 13, 742). When the action takes place at  $120\text{--}130^\circ$ , then a reddish viscid liquid is formed, from which a crystalline compound,  $\text{C}_8\text{H}_7\text{NBr}$ , may be obtained. It is insoluble in most solvents save glacial acetic acid, and is decomposed by water and alkalis. At  $200^\circ$  it melts with decomposition. When heated with concentrated hydrochloric acid at  $150^\circ$ , it yields an oily liquid, apparently phenylbromacetic acid, whereas with dilute hydrochloric acid it yields mandelic acid, thus:



This crystalline product forms about 15 per cent. of the benzyl cyanide used; the oil from which it crystallises, which is soluble in

ether, appears to be phenylbromacetonitril,  $\text{CHPhBr.CN}$ , and when heated at  $170\text{--}180^\circ$ , yields stilbene dicyanide. It is more easily converted into stilbene dicyanide by the action of an alcoholic solution of potassium cyanide. If an excess of potassium cyanide is used, the product contains some dibenzylene dicyanide,  $\text{C}_{14}\text{H}_{12}(\text{CN})_2$ ; it is separated from the stilbene dicyanide by its comparative insolubility in chloroform; m. p.  $214^\circ$ . Dibenzylene dicyanide (m. p.  $218^\circ$ ) is obtained from stilbene dicyanide by the action of sodium-amalgam on acid solutions, or zinc and hydrochloric acid.

Phenylbromacetonitril is converted into potassium stilbenedicarboxylate by alcoholic potash, and if the reaction takes place in the cold, stilbenedicarbonimide is obtained. Stilbenedicarboxylic anhydride (prepared from potassium stilbenedicarboxylate by the action of acids) dissolves in nitric acid, forming a dinitrostilbenedicarboxylic anhydride,  $\text{C}_{16}\text{H}_8\text{O}_3(\text{NO}_2)_2$ ; it is insoluble in water, sparingly soluble in alcohol, and easily soluble in chloroform: it has not been obtained in a crystalline form. On oxidation, it forms paranitrobenzoic acid only, showing that the nitro-group is in the para-position in both nuclei. When reduced, it yields diamidodibenzylidicarboxylic acid, crystallising in tablets, m. p.  $280^\circ$ .

Amongst the products of the action of bromine on benzyl cyanide at  $160\text{--}180^\circ$ , is one which is insoluble in benzene; it crystallises in golden-yellow silky needles, m. p.  $242^\circ$ ; it is isomeric with stilbene dicyanide. It is slowly acted on by alcoholic potash, and is thereby converted into an acid having the formula  $\text{COOH.C}_{14}\text{H}_{10}.\text{CN}$  (m. p.  $222^\circ$ ). By the action of hydrochloric acid, this body is converted into an indifferent substance still containing nitrogen. P. P. B.

**Preparation of Benzyl Alcohol.** By R. MEYER (*Ber.*, **14**, 2394—2396).—In preparing benzyl alcohol from benzaldehyde, a better yield is obtained by using an aqueous instead of an alcoholic solution of potash. It is advisable to distil benzyl alcohol before drying, as it unites with calcium chloride and is attacked by solid potash. Benzyl alcohol is soluble in 25 parts of water. W. C. W.

**Parabromobenzyl Compounds.** By C. L. JACKSON and W. LOWERY (*Am. Chem. J.*, **3**, 247—252).—*Parabromobenzyl alcohol*,  $\text{C}_6\text{H}_4\text{CH}_2\text{OH.H.H.Br.H}_2$ , and several of its ethers were described by the authors in 1879 (*Ber.*, **10**, 1209; *Chem. Soc. J.*, 1880, Abstr., 64). The bromide treated in the cold with alcoholic ammonia yields a mixture of three parabromobenzylamines, or their hydrobromides, from which the bases may be obtained by washing out the hydrobromide of the primary amine with water, treating the residue with caustic soda, and separating the secondary from the tertiary amine by crystallisation from alcohol.

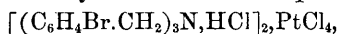
The *primary amine*,  $\text{C}_6\text{H}_4\text{Br.CH}_2.\text{NH}_2$ , is an oil which is soluble in ether, may be distilled with steam, and on exposure to the air, is quickly converted into a *carbonate*, which crystallises in radiate groups of small white prisms (m. p.  $131\text{--}133^\circ$ ), soluble in water and in alcohol, insoluble in ether, benzene and carbon bisulphide. The *hydrochloride* forms flattened needles, melting with apparent decomposition at  $260^\circ$ . The *platinochloride*,  $[\text{C}_6\text{H}_4\text{Br.CH}_2.\text{NH}_2.\text{HCl}]_2.\text{PtCl}_4$ , crystal-

lises in groups of orange-yellow plates, apparently monoclinic, slightly soluble in cold, more freely in hot water and in alcohol.

The *secondary amine*,  $(\text{C}_6\text{H}_4\text{Br}.\text{CH}_2)_2\text{NH}$ , is left, on evaporating its alcoholic solution, as an oil, which solidifies on stirring, and may be crystallised. It melts at  $50^\circ$  and dissolves readily in alcohol and in ether.

The *hydrochloride* forms glistening rhombic plates melting at  $283^\circ$ . The *platinochloride*,  $[(\text{C}_6\text{H}_4\text{Br}.\text{CH}_2)_2\text{NH}.\text{HCl}]_2.\text{PtCl}_4$ , is a yellow powder nearly insoluble in water and in alcohol.

The *tertiary amine*,  $(\text{C}_6\text{H}_4\text{Br}.\text{CH}_2)_3\text{N}$ , purified by crystallisation from ether or from light petroleum, forms matted or radiate groups of white slender needles, insoluble in water, very slightly soluble in alcohol, either hot or cold, somewhat sparingly in warm ether, but freely in hot light petroleum. Its melting point varies according to the solvent from which it separates, the crystals from petroleum melting at  $92^\circ$ , whereas those from common ether melt at  $76$ – $78^\circ$ . It does not appear to form a definite hydrochloride. The *platinochloride*,



prepared by adding chloroplatinic acid to a solution of the base in ether, forms corn-yellow indistinct crystals, insoluble or nearly so in all the common solvents. H. W.

**Synthesis of Phenols.** By A. LIEBMANN (*Ber.*, **14**, 1842–1844). The higher homologues of phenol cannot be obtained by the action of chlorine derivatives of the hydrocarbons on the phenols, but their preparation can be effected by the action of zinc chloride on a mixture of the phenols and alcohols. Thus from phenol and isobutyl alcohol, a butylphenol,  $\text{C}_4\text{H}_9.\text{C}_6\text{H}_4.\text{OH}$  (m. p.  $98^\circ$ , b. p.  $236$ – $238^\circ$ ) is obtained, as a snow-white crystalline mass; it dissolves in alkalis, forming salts sparingly soluble in cold, readily soluble in hot water. This butylphenol is probably identical with that obtained from butyl aniline by Studer (*Abstr.*, 1881, 898); its ethyl ether boils at  $234$ – $236^\circ$ .

By a similar process, amylphenol (m. p.  $92^\circ$ , b. p.  $248$ – $250^\circ$ ) and benzylphenol (b. p.  $314$ – $316^\circ$ ) have been prepared, and further researches with resorcinol, orcinol,  $\alpha$ - and  $\beta$ -naphthol are promised. These higher homologues of phenol differ, however, from phenol in giving no coloration with ferric chloride. V. H. V.

**Action of Benzyl Chloride and Zinc on Natural Thymol.** By G. MAZZARA (*Gazzetta*, 1881, 346–352, and 433–436).—*Monobenzylthymol*,  $\text{C}_{17}\text{H}_{20}\text{O} = \text{C}_6\text{H}_2(\text{OH})(\text{CH}_3)(\text{C}_3\text{H}_7)(\text{CH}_2.\text{C}_6\text{H}_5)$  is prepared by gently heating in a capacious flask, equal parts of benzyl chloride and thymol (70 grams of each) with 10–15 grams of zinc-turnings or filings. Hydrogen chloride is then abundantly evolved, and the liquid begins to boil, acquiring first a red, then a red-brown colour, the action continuing for 15 to 20 minutes, after which a stronger heat must be employed to complete it. The product must be purified by distillation in a vacuum, as under ordinary pressure the portions of thymol and benzyl chloride which have not taken part in the reaction cannot be distilled off without altering it. The portions distilling below  $200^\circ$  having passed over, the thermometer quickly rises to  $240$ —

260°, between which limits a yellow oily liquid distils over, and there remains in the retort a black liquid, which boils at 280° under the pressure above mentioned, but distils over with difficulty. The distillate obtained between 240° and 260° forms, after several fractional distillations, a yellowish-white liquid, boiling under a pressure of 8 mm. at 255°. This product is, however, still a mixture of mono- and di-benzylthymol, but after a further series of fractionations, rejecting always the first and last portions of the distillate, the monobenzyl compound is obtained quite pure.

Monobenzylthymol is a liquid, having a faint phenolic odour. When cooled by a mixture of ice and salt, it does not solidify, but becomes so viscid as not to run out when the containing vessel is inverted. It likewise remains liquid when separated from its alcoholic or ethereal solution by slow evaporation. Small crystals have, however, been observed to form in it after long standing. It dissolves in alcohol, ether, chloroform, benzene, &c., but is insoluble in water. With solution of ferric chloride, it gives a yellowish colour, changing to deep red on boiling. It does not dissolve in caustic potash-ley, even at boiling heat, and is likewise insoluble in ammonia and alkaline carbonates; but its phenolic character is manifested on heating it with sodium, whereupon hydrogen is evolved, and sodium-benzylphenol is formed, which is decomposed by water, with reproduction of the phenol.

The *acetyl-derivative*,  $C_6H_2(OC_2H_5O)(CH_3)(C_3H_7)(CH_2C_6H_5)$ , is formed on mixing benzylphenol with excess of acetic chloride in a reflux apparatus. The action begins in the cold, but requires the aid of heat to complete it. On distilling the product, first under ordinary pressure to remove the excess of acetic chloride, and then in a vacuum, the acetyl-benzylphenol is obtained as a colourless liquid, boiling at 245° under a pressure of 8 mm. It has a faint acetic odour, and, like the phenol itself, does not solidify in a mixture of snow and salt. Heated with potash-solution or with water, it decomposes, reproducing the phenol.

In attempting to prepare the acid,



by the action of sodium and  $CO_2$  on the phenol, the author obtained an acid which separated from its ammoniacal solution in small white needles; but the quantity was too small for examination.

*Dibenzyl-thymol*,  $C_6H(OH)CH_2(C_3H_7)(C_7H_7)_2$ , is formed, as above stated, in the preparation of monobenzyl-thymol, and remains in the retort, after the latter has distilled over, in the form of a black liquid, which boils at 280° under 8 mm., but distils over with difficulty. On cooling, however, it solidifies to a mass of crystals impregnated with a viscid substance, and may be purified by boiling it with dilute alcohol, leaving the solution to cool down to a tepid warmth, and then filtering, taking care not to allow the oily substance which begins to separate after boiling, to fall upon the filter. The filtrate on cooling deposits crystals, which may be freed from a small quantity of oily matter by spreading them out on bibulous paper, and further purified by a few recrystallisations from alcohol.

Dibenzyl-thymol crystallises from dilute alcohol in prismatic laminæ

or needles, perfectly white and having a splendid silky lustre; from strong alcohol it separates in a mass of needles. When quite pure it is nearly inodorous. It is not altered by exposure to air or light; dissolves in ether, acetic acid, and chloroform, but is insoluble in water, potash, ammonia, and alkaline carbonates. With ferric chloride it reacts like monobenzyl-thymol. It melts at  $76^{\circ}$ , and after fusion in capillary tubes, solidifies at ordinary temperature. When heated in small flasks under a pressure of 6 to 8 mm., it distils with partial decomposition.

*Acetyl-dibenzyl-thymol*,  $C_6H(OC_2H_3O)(CH_3)(C_3H_7)(C_7H_7)_2$ , is obtained by the action of acetic chloride on dibenzyl-thymol, as a dense viscid liquid, solidifying on cooling in crystals, which appear under the microscope as fan-shaped groups of small micaceous needles. It has a faint acetic odour, dissolves in boiling alcohol, and separates on cooling in shining prismatic needles. It is permanent in dry air, melts at  $82-85^{\circ}$ , and solidifies after a while at ordinary temperature. It is decomposed by aqueous potash at the boiling heat, yielding a substance having the composition of the original dibenzyl-thymol, but melting at a much higher temperature, viz., at  $112^{\circ}$ . The author intends to submit this new modification to further examination.

*Methylic Ether of Dibenzylthymol*,  $C_6H(CH_3)(C_3H_7)(C_7H_7)_2.OCH_3$ .—This compound is prepared by adding methyl iodide to a solution of thymol and potash in methyl alcohol, all these substances being used in the proportions required by calculation. Reaction soon begins at the ordinary temperature, but to complete it, the mixture must be heated in the water-bath for two hours. On subsequently adding water, an oily liquid separates, which does not solidify for a long time, and may be separated from the watery liquid by treating the whole with ether, separating the ethereal layer by a tap-funnel, evaporating off the ether on the water-bath, heating the residue in an oil-bath to drive off the water, and finally distilling it over an open fire under reduced pressure. The product thus obtained is a dense yellowish liquid, which has a characteristic odour, and when cooled by a mixture of ice and salt, becomes viscid, and after some time, solidifies to a mass of prismatic crystals. It may be purified by two crystallisations from boiling absolute alcohol, from which it separates in long, hard, shining prisms, perfectly white and scentless. It is moderately soluble in ether, insoluble in water, and separates from aqueous alcohol in the liquid form.

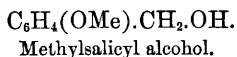
*The benzoic ether*,  $C_6H(CH_3)(C_3H_7)(C_7H_7)_2(OC_7H_5O)$ . This compound is prepared by heating a mixture of benzyl chloride and dibenzylthymol, as long as hydrogen chloride continues to be evolved. The product, which does not solidify even after long standing, may be purified by washing it in cold dilute potash and then dissolving it in a mixture of alcohol and ether, from which it separates in the liquid state, but solidifies after a few days to a mass of needles. On redissolving these, however, in alcohol and ether, the compound again separates in the liquid state, and solidifies only after long standing. It begins to soften at  $60^{\circ}$ , and melts at  $75-80^{\circ}$ . It is insoluble in water, but dissolves in ether and in alcohol, especially when concentrated. It has a peculiar odour, recalling that of benzoic acid.

H. W.

**Derivatives of Saligenol.** By K. BÖTSCH (*Monatsh. Chem.*, **2**, 621—623).—*Ethylsalicyl alcohol*,  $C_9H_{12}O_2 = C_6H_4OEt.(CH_2.OH)$ , is prepared—like its lower homologue, methylsalicyl alcohol, discovered by Cannizzaro and Körner (this Journal, 1872, p. 1095), by heating potassium-saligenol, dissolved in water, with the theoretical quantity of ethyl iodide in a sealed vessel for three hours at  $100^\circ$ ; it is purified by agitation with sulphurous acid, potassium carbonate, and water in succession, and, finally, by fractionation. This last process must be performed with great caution, as the alcohol has a strong tendency to resinise, especially if the temperature rises a little above the boiling point, or if traces of potassium iodide are present.

Ethylsalicyl alcohol is a colourless liquid having a pleasant ethereal odour, boiling at  $265^\circ$ , solidifying to a crystalline mass at  $0^\circ$ , but liquefying again on slight rise of temperature. It is insoluble in water, but dissolves readily in alcohol and in ether; the alcoholic solution does not give any colour-reaction with ferric chloride. On prolonged exposure to the air, it becomes dark-coloured, and appears to decompose. By oxidation with dilute nitric acid, it is converted into ethylsalicylic acid. With strong hydrochloric acid, in a sealed tube, it yields ethyl chloride and saligenol, which is immediately resolved into water and saliretin.

*Methylsalicyl alcohol*,  $C_8H_{10}O_2$ , is isomeric with Bernheimer's caffeol, obtained by the roasting of coffee (p. 231). The reaction of this latter compound with alcoholic potash, and with hydriodic acid and phosphorus, and the formation of palmitic acid by fusing it with potash, show that it is a derivative of saligenol. Cannizzaro and Körner, who discovered methylsalicyl alcohol, say nothing about its odour. Bötsch, however, on preparing it in the manner above mentioned, finds that the crude product has a decided odour of roasted coffee, which, however, disappears completely on purification: whence it follows that caffeol cannot be identical with methylsalicyl alcohol. The two isomeric compounds may most probably be represented by the following formulæ:—



It is possible, however, that traces of caffeol may be formed in the preparation of methylsalicyl alcohol, and give rise to the odour of the crude product.

H. W.

**Synthesis of Methylarbutin.** By A. MICHAEL (*Ber.*, **14**, 2097—2102).—Starting on the hypothesis that arbutin is a mixture of the glucosides of quinol and methylquinol, the author tried to make it by the action of acetochlorhydrose on the potassium salts of these substances; he, however, succeeded only in finding methylquinol glucoside.

The methylquinol used was obtained from arbutin (m. p.  $168-169^\circ$ ) by Hlasiwetz and Habermann's method, that is, by pouring alcoholic potash into an alcoholic solution of arbutin, and treating the precipitate with hydrochloric acid. For the preparation of the glucoside, the potassium salt is dissolved in absolute alcohol and mixed with

less than 1 mol. acetochlorhydrose, being at the same time cooled; after two days the product is filtered, and the filtrate after several days deposits white crystals,  $2C_{13}H_{18}O_7 + H_2O$ , which are purified by crystallisation, &c.: it crystallises in tufts of colourless needles having a silky lustre and bitter taste, losing their water at  $120^\circ$ , melting at  $168$ — $169^\circ$ , solidifying at  $137$ — $135^\circ$ , soluble in water and alcohol, only slightly in ether. The aqueous solution is not precipitated either by basic lead acetate or by copper sulphate, or by Fehling's solution; neither was it coloured blue by ferric chloride (showing absence of free hydroxyl group). It dissolves in strong nitric acid to a yellow solution, which, mixed with sulphuric acid and alcohol, diluted, and treated with an excess of potash, becomes violet. It decomposes when heated with dilute mineral acids, giving grape-sugar and methylquinol; and, with dilute sulphuric acid and manganese dioxide, it evolves the penetrating odour of benzoquinone. The author thinks that these properties of methylquinol glucoside speak decisively in favour of the above hypothesis. The melting point he obtained differs from Schiff's (Abstr., 1881, 610).

In the residues from his worked-up arbutin, the author obtained a body (m. p.  $140^\circ$ ) which, after being several times recrystallised, resolved itself into two bodies, melting respectively at  $138^\circ$  and  $146^\circ$ ; both give quinol as well as methylquinol on being decomposed by acids. The author proposes a constitutional formula for helicin, which is based on the assumption that grape-sugar does not owe its reducing properties to the formyl-group, but probably to one of the secondary carbinol-groups.

D. A. L.

**Attempted Synthesis of Pyrogallol.** By G. MAGATTI (*Gazzetta*, 1881, 353—357).—The three hydroxyl-groups in this compound are generally supposed to occupy the position 1, 2, 4; but this view, resting solely on the conversion of dibromo- or diiodo-salicylic acid, or of the two orthophenolsulphonic acids, into pyrogallol by the action of melting potash, cannot, for well-known reasons, be regarded as satisfactorily established. The author has therefore attempted to demonstrate the constitution of pyrogallol by a different process, viz., by converting Habermann's nitrodimethylquinol (Abstr., 1878, 728) into the corresponding amido-compound,  $C_6H_3(NH_2)(OMe)_2$ , which crystallises in white needles melting at  $80^\circ$ , and turning red at the same time; this into the diazo-compound; and decomposing this latter with water. By this process a few drops of a viscid reddish liquid were obtained having the characteristic odour of Hofmann's pyrogallic ethers, but the quantity obtained was too small for satisfactory examination. It will be seen, therefore, that this method, like those previously tried, has not led to any conclusive demonstration of the constitution of pyrogallol.

H. W.

**Reactions of Dimethylaniline.** By W. MICHLER and H. WALDER (*Ber.*, 14, 2175—2177).—Dimethylaniline is converted into diamidodiphenylmethane by the action of phosphorus pentachloride.

On adding sodium nitrite to the calcium salt of dimethylaniline-sulphonic acid, a golden precipitate of mononitrodimethylaniline is thrown down which, after suitable purification, crystallises in golden



leaflets. On treating the filtrate with ammonia, evaporating, and adding hydrochloric acid, *nitrodimethylanilinesulphonic acid* is precipitated. The *barium* and *calcium* salts of this acid form rhombic crystals sparingly soluble in water. By reduction of the nitro-acid with tin and hydrochloric acid, the corresponding *amido-acid* is obtained, crystallising in large rhombohedra; its *barium* and *calcium* salts crystallise in glistening leaflets.

By the action of concentrated sulphuric acid on monobromodimethylaniline at 100°, dimethylanilinesulphonic acid is formed.

V. H. V.

**Butylation of Aniline.** By A. STUDER (*Ber.*, **14**, 2186—2188).—The author has prepared some of the derivatives of amidobutylbenzene (Abstr., 1881, 898); the hydriodide crystallises in golden, the hydrobromide in glistening white needles. In the preparation of amidobutylbenzene there is also formed some quantity of a more highly substituted derivative, which is probably a mixture of isomerides of the composition  $4C_4H_9N.C_6H_4.C_4H_9$ .

*Butylanisole*, prepared by the action of methyl iodide on potassium butylphenol, is a colourless, strongly refractive oil (b. p. 215.5, sp. gr. 0.9368).

*Benzoylbutylphenol*, formed from butylphenol and benzoic chloride, crystallises in large white leaflets (m. p. 83°, b. p. 335°).

*Acetylbutylphenol*, from butylphenol and acetic chloride, is a colourless oil (b. p. 245°, sp. gr. 0.999).

As Engelhardt and Latschinoff have shown that thymol is decomposed by phosphoric anhydride into metacresol and propylene, the author has studied the analogous decomposition of the isomeric butylphenol. On passing the gas given off into a solution of bromine in potassium bromide, isobutylene bromide was obtained, whilst the residue, on saponification and distillation in a current of steam, gave only phenol.

V. H. V.

**Benzoylaniline.** By O. DOEBNER and G. WEISS (*Ber.*, **14**, 1836—1842).—The authors have more fully investigated the chemical properties of benzoylaniline, the preparation of which from benzoic chloride and phthalylanilide has already been described (Abstr., 1880, 304). The base is monacid, combining with acids to form well-crystallised compounds. On heating 1 mol. of the base with 3 mols. of methyl iodide, benzodimethylaniline methiodide,  $Bz.C_6H_4.NMe_3I$ , is obtained in large silky glistening tables; at 181° this compound melts and is decomposed into methyl iodide and *benzoyldimethylaniline*. The latter crystallises in colourless leaflets (m. p. 90°), and is identical with the benzoyldimethylaniline obtained by the action of concentrated hydrochloric acid on malachite-green (Abstr., 1879, 312). *Acetylbenzoylaniline*,  $Bz.C_6H_4.NHAc$ , prepared from benzoylaniline and acetic chloride, crystallises in long needles (m. p. 153°), insoluble in water, soluble in alcohol and ether. *Benzobenzoylaniline*,  $Bz.C_6H_4.NH.Bz$ , forms colourless glistening leaflets (m. p. 152°), insoluble in water, soluble in alcohol. *Benzoylphenylcarbamine*,  $Bz.C_6H_4.NC$ , is prepared by the action of alcoholic chloroform on benzoylaniline. It forms

colourless needles (m. p. 118°), insoluble in water, easily soluble in alcohol, ether, benzene, &c. *Benzoylphenylmethane*,



is prepared by the action of benzylaniline on ethyl chlorocarbonate. It forms glistening leaflets (m. p. 189°), insoluble in water, soluble in alcohol, ether, &c. *Benzoylphenylthiocarbamide*,  $(\text{Bz.C}_6\text{H}_4.\text{NH})_2\text{CS}$ , is obtained by heating benzylaniline with excess of carbon bisulphide; it forms colourless glistening leaflets (m. p. 166°), insoluble in water, soluble in alcohol, ether, benzene, &c. By the action of nitrous acid, benzylaniline is converted into *benzoylphenol*,  $\text{Bz.C}_6\text{H}_4.\text{OH}$ , which crystallises in colourless needles (m. p. 134°), and is identical with the benzoylphenol obtained from benzoic chloride and phenol. On melting benzylaniline with zinc chloride, a molecule of water is given off, and a nitril,  $\text{C}_{13}\text{H}_9\text{N}$ , is obtained which crystallises in glistening leaflets (m. p. 118°), insoluble in water, soluble in alcohol, ether, and benzene;

its constitution is probably  $\text{N} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{CPh} \end{array}$ .

V. H. V.

**Diamidotolyl Compounds.** By W. MICHLER and A. SAMPAIO (*Ber.*, 14, 2167—2175).—When orthodimethyltoluidine is heated with sulphuric acid, it yields products analogous to those from dimethylaniline, viz., *dimethyltoluidinesulphonic acid*,



and *tetramethyldiamidotolyl*,  $\text{Me}_2\text{N.C}_6\text{H}_3\text{Me.C}_6\text{H}_3\text{Me.NMe}_2$ . The former crystallises in large glistening prisms insoluble in alcohol, soluble in hot water; its *barium* salt crystallises in stellate leaflets, the *calcium* salt in small druses, and the *zinc* salt in easily soluble needles.

The separation of the tetramethyldiamidotolyl from the crude product of the reaction alone presents some difficulty, owing to the fact that it does not readily crystallise from the resinous products formed; it is best prepared by precipitating the crude product with potassium ferrocyanide, and decomposing the ferrocyanide of the base with soda. Tetramethyldiamidotolyl forms long needles (m. p. 190°), sparingly soluble in alcohol, perfectly insoluble in water; its *hydrochloride*,  $[\text{C}_6\text{H}_3\text{Me.NMe}_2]_2\text{HCl}$ , crystallises in large white needles; its *platinochloride* is a golden, delicate, crystalline precipitate. Tetramethyldiamidotolyl may also be obtained by the oxidation of orthodimethyltoluidine with manganese dioxide, or by the direct action of methyl alcohol on orthodimethyltoluidine in presence of hydrochloric acid.

Orthobromodimethyltoluidine, prepared either by the action of bromine on orthodimethyltoluidine in acetic acid solution, or by the methylation of bromorthotoluidine, is a colourless heavy liquid (b. p. 244°), insoluble in water, soluble in alcohol and ether. Bromorthodimethyltoluidine behaves towards sulphuric acid like orthodimethyltoluidine, yielding a dibromo-derivative of tetramethyldiamidotolyl; the substance crystallises in large white needles (m. p. 117°), insoluble in water, soluble in hot alcohol and ether. Orthobromodimethyl-

toluidine, when oxidised with sulphuric acid and manganese dioxide, yields a product identical in chemical and physical properties with the tetramethyldiamidotolyl melting at 80°. V. H. V.

**Action of Phosphorus Pentachloride on Acetyl- and Benzoyl-diphenylamine.** By A. CLAUS (*Ber.*, **14**, 2365—2375).—*Dichlorobenzenyldiphenylamine*,  $\text{NPh}_2\text{CCl}_2\text{Ph}$ , is formed by the action of phosphorus pentachloride on benzoyldiphenylamine at 100°. The crude product is dissolved in chloroform, and the solution repeatedly shaken with water to remove phosphorus compounds. On evaporating the chloroform, colourless needle-shaped crystals remain (m. p. 149°).

If acetyldiphenylamine is substituted for benzoyldiphenylamine in the preceding reaction, a continuous evolution of hydrochloric acid takes place, and no dichloride is formed. When the solution of the crude product in chloroform is shaken with water, a crystalline phosphorus compound is deposited from the aqueous solution. The crystals have the composition  $\text{C}_{12}\text{H}_{10}\text{N} \cdot \text{C}_2\text{H}_3\text{Cl} \cdot (\text{PO}_3\text{H}_2) + 2\text{H}_2\text{O}$ .

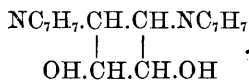
The oily liquid obtained by the action of phosphorus pentachloride (1 mol.) on acetyldiphenylamine (2 mols.) deposits needle-shaped crystals (m. p. 186°) on the addition of alcoholic ammonia. The new compound has the composition  $\text{C}_{28}\text{H}_{30}\text{N}_4\text{O}$ . It is decomposed by platinum chloride, ammonium platinochloride being precipitated and a substance of the composition  $\text{C}_{28}\text{H}_{28}\text{N}_4\text{O}_3$  being formed. This body crystallises in glistening needles (m. p. 85°). W. C. W.

**Dry Distillation of the Mucates of Aromatic Amines.** By L. LICHTENSTEIN (*Ber.*, **14**, 2093—2097).—This is in continuation of a former communication (*Abstr.*, 1881, 722). The name *toluylpyrrol* is proposed for the body  $\text{C}_{11}\text{H}_{11}\text{N}$ , because it was derived from a toluidine salt, and *tetrolodianil* and *tetrolditolyl* respectively for  $\text{C}_{16}\text{H}_{14}\text{N}_2$  and  $\text{C}_{18}\text{H}_{18}\text{N}_2$ , because they can be regarded as compounds of the hypothetical hydrocarbon tetrol  $\text{C}_4\text{H}_4$ , with 2 mols. of the radicle anil  $\text{C}_6\text{H}_5\text{N}$ , or tolil  $\text{C}_7\text{H}_7\text{N}$ .

Tetrolditolyl oxidised with chromic mixture yields a body,  $\text{C}_{18}\text{H}_{19}\text{NO}$ . The product of the action of ammonium sulphite on brominated tetrolditolyl has been analysed again, and gives numbers for



While distilling some toluidine mucate, fine slender white needles collected in the upper part of the retort; these are insoluble in alcohol, ether, naphtha, and benzene, and have the formula  $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_2$ , which is that of tetrolditolil plus 2 mol.  $\text{H}_2\text{O}$ . It is probably



Diphenylamine with mucic acid, treated in the same way as aniline, does not combine with it; the author therefore adopted Altmann's method. The product of the distillation of potassium mucate and diphenylamine,  $\text{C}_{20}\text{H}_{26}\text{N}_2$ , is a white crystalline body soluble in most solvents except water. When heated with nitric acid, sp. gr. 1.13,

it dissolves to a clear yellow solution which on further heating suddenly turns black; on diluting it becomes yellow. With a mixture of nitric and hydrochloric acids a violet colour, turning to red, is produced, and, after 24 hours, a grey-green precipitate is formed. Bromination and oxidation experiments on this substance yielded unfavourable results.

The mucates of orthotoluidine, naphthylamine, and benzidine are completely decomposed by dry distillation, whilst dimethylaniline and methyldiphenylamine distil unchanged from potassium mucate.

D. A. L.

**Preparation of Amines from Phenols and Alcohols.** By V. MERZ and W. WEITH (*Ber.*, **14**, 2343—2347).—When  $\beta$ -naphthol is treated at  $280^\circ$  with an excess of ammonium acetate,  $\beta$ -acetonaphthalide,  $\beta$ -naphthylamine, and small quantities of  $\beta$ -dinaphthylamine are formed. In presence of glacial acetic acid,  $\beta$ -acetonaphthalide is almost the sole product. The addition of zinc chloride to the  $\beta$ -naphthol increases the yield of dinaphthylamine. As  $\beta$ -acetonaphthalide is easily decomposed by hot dilute sulphuric acid, the naphthylamine can easily be isolated. When  $\alpha$ -naphthol is substituted for  $\beta$ -naphthol, a smaller yield of naphthylamine is obtained.

The chief product of the action of ammonia calcium chloride on  $\alpha$ - or  $\beta$ -naphthol is the corresponding mononaphthylamine, but when ammonia zinc chloride is used, dinaphthylamine is the chief product.

Almost the theoretical yield of *paratolyl* or *phenyl- $\beta$ -naphthylamine* is obtained by the action of aniline or paratoluidine calcium chloride on  $\beta$ -naphthol. With  $\alpha$ -naphthol less favourable results are obtained. Paratolyl  $\beta$ -naphthylamine crystallises in glistening scales (m. p.  $102^\circ$ ), freely soluble in hot alcohol and in light petroleum.

Phenylparatolylamine can be prepared by the action of paratoluidine zinc chloride on phenol or of aniline zinc chloride on paracresol at  $250^\circ$ , and also by heating a mixture of aniline and paracresol with antimony trichloride.

Resorcinol is converted into *metoxydiphenylamine*,  $\text{NHPh.C}_6\text{H}_4.\text{OH}$ , by treatment with ammonia calcium chloride at  $270^\circ$ . This body crystallises in white plates or needles (m. p.  $82^\circ$ ), and forms crystalline compounds with potassium, sodium, barium, &c.

Aniline zinc chloride acts on ordinary amyl alcohol, yielding amido-amylbenzene,  $\text{NHPh.C}_5\text{H}_{11}$ .

W. C. W.

**Reaction of Organic Compounds with Rosaniline Sulphite.** By J. G. SCHMIDT (*Ber.*, **14**, 1848—1851).—The researches of Schiff (*Compt. rend.*, **64**, 482) and of Caro have established that aldehydes give a characteristic violet reaction with a solution prepared by treating rosaniline salts with acid sodium sulphite and sulphuric acid. The author has observed this reaction with many aldehydes or compounds of an aldehydic nature, and finds that it is a general characteristic of this class. Attention is drawn to the fact that although chloral gives this reaction, chloral hydrate does not, which lends support to the view that the latter compound is of the nature of a glycol, and is not a molecular combination of chloral and water. Among other classes of compounds, acetone, and methyl and ethyl

alcohols freshly distilled from ammoniacal silver solution, so as to ensure the absence of aldehyde, give the violet tint, but the higher homologues are without action.

V. H. V.

**Preparation of Carbotriphenylamine.** By W. MICHLER and H. WALDER (*Ber.*, 14, 2174—2175).—If 4 parts of aniline be added gradually to 1 part of trichloromethylsulphochloride, the crude product decomposed by water, the unattacked aniline distilled off in a current of steam, and the residue dissolved in hydrochloric acid, it gives a compound identical in chemical and physical properties with the hydrochloride of carbotriphenylamine. This reaction shows that trichloromethylsulphochloride undergoes a decomposition analogous to that of tetrachloromethane (*Abstr.*, 1879, 920).

V. H. V.

**Anhydro-compounds** (Continuation). By H. HÜBNER (*Annalen*, 209, 339—384).—The diphenyl derivatives have already been described by A. Osten (*this Journal*, 1874, 580) and by Lüddens (*this Journal*, 1875, 1258). See also *Watts's Dictionary*, Suppl. 2, p. 937, and Suppl. 3, p. 660.

*Ethenylphenylenediamine*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{CMe}$  (m. p. 170°), is prepared

by treating a solution of acetorthonitranilide in glacial acetic acid with metallic tin (*Ber.*, 8, 677), or by the reduction of bromonitracetanilide with tin and hydrochloric acid (*this Journal*, 1873, 1147; 1874, 78).

Friederici has pointed out (*Abstr.*, 1879, 311) that nitrotrichloracetotoluide does not give an anhydro base on reduction, but forms toluylene-diamine. *Metanitroparavaleryltoluide* (m. p. 88°), on reduction with tin and hydrochloric acid, yields *anhydrovaleryldiamidotoluene*,

$\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{C.C}_4\text{H}_9$ . This base crystallises in prisms (m. p. 145°),

which are freely soluble in alcohol. It does not form crystalline salts.

*Anhydro-bases from Dibasic Acids.*—Oxaldinitranilide,



is deposited in crystalline plates (m. p. 260°), when strong nitric acid is slowly added to a solution of oxanilide in glacial acetic acid. This substance is insoluble in alcohol, ether, and chloroform. It yields paradiamidobenzene on reduction, but no anhydro-base.

By the action of anhydrous oxalic acid on orthonitraniline at 130°, a mixture of oxalorthonitranilic acid, ethyl oxalorthonitranilate, and oxalorthonitranilide is produced. If the product is extracted with alcohol and afterwards with acetic acid, oxalorthonitranilide remains undissolved. On evaporating the alcoholic and acetic acid extracts, oxal-nitranilic acid,  $\text{C}_6\text{H}_4(\text{NO}_2).\text{NH}(\text{CO}).\text{COOH} + 2\text{H}_2\text{O}$ , is deposited in silvery needles, soluble in water, acetic acid, and in soda-lye. The mother liquor contains the ethylic salt of this acid,  $\text{C}_6\text{H}_4(\text{NO}_2).\text{NH}(\text{CO}).\text{COOEt}$  (m. p. 112°), which crystallises in yellow needles, soluble in alcohol, ether, petroleum, carbon bisulphide, glacial acetic acid, benzene, and acetone.

*Oxalorthonitranilide*,  $[\text{C}_6\text{H}_4(\text{NO}_2).\text{NH}_2]_2\text{C}_2\text{O}_2$ , forms needles of a pale yellow colour, freely soluble in aniline. It melts above  $300^\circ$ , and sublimes with partial decomposition.

*Formorthonitranilide*,  $\text{C}_6\text{H}_4(\text{NO}_2).\text{NH}.\text{COH}$ , prepared by boiling orthonitraniline with anhydrous formic acid, crystallises in yellow needles (m. p.  $122^\circ$ ), which dissolve freely in alcohol, ether, carbon bisulphide, benzene, chloroform, acetone, glacial acetic acid, and hot water.

*Anhydroxanilide*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{NH} \end{array} \text{C}_6\text{H}_4$ , prepared by treat-

ing a concentrated solution of oxorthonitranilide in glacial acetic acid with metallic tin, forms yellow needles, freely soluble in glacial acetic acid. The base does not melt at  $300^\circ$ , but can be volatilised without decomposition. It forms crystalline salts with hydrochloric, nitric, and sulphuric acids.

*Ditolyloxamide*,  $(\text{C}_6\text{H}_4\text{Me}.\text{NH})_2\text{C}_2\text{O}_2$ , is a colourless crystalline body (m. p.  $263^\circ$ ), soluble in hot acetic acid. By the action of strong nitric acid, it is converted into the dinitro-derivative, which yields *anhydroxaltoluidide*,  $\text{C}_{16}\text{H}_{14}\text{N}_4$ , on reduction with tin and acetic acid. This base melts about  $193^\circ$ , and does not form a crystalline hydrochloride or sulphate.

*Ortho- and para-nitrophenyl succinimides* (m. p.  $156^\circ$  and  $205^\circ$  respectively) have been previously described by Taylor (this Journal, 1876, 602). On reduction with tin and aqueous hydrochloric acid, they are converted into succinic acid and diamido-benzene; but on treating orthonitrophenylsuccinimide with glacial acetic acid saturated with hydrochloric acid gas, an unstable base,  $\text{C}_6\text{H}_4(\text{NH}_2).\text{N}(\text{CO}.\text{C}_2\text{H}_4.\text{CO})$ , is formed, which is rapidly converted into the anhydro-compound

$\text{C}_6\text{H}_4 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{N} \end{array} \text{C}_2\text{H}_4\text{CO}$ . This anhydro-derivative unites with 2 mols.  $\text{HCl}$  to form a colourless crystalline salt.

*Succindinitranilide*  $[\text{C}_6\text{H}_4(\text{NO}_2).\text{NH}_2]_2\text{C}_4\text{H}_4\text{O}_2$ , forms yellow needle-shaped crystals, soluble in aniline.

*Tolylsuccinimide*,  $\text{C}_6\text{H}_4\text{Me}.\text{N}.\text{C}_4\text{H}_4\text{O}_2$  (m. p.  $150^\circ$ ), and its nitro-derivative,  $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2).\text{N}.\text{C}_4\text{H}_4\text{O}_2$  (m. p.  $140^\circ$ ), have been described by Taylor (*loc. cit.*). *Ditolylsuccinimide*,  $(\text{C}_6\text{H}_4\text{Me}.\text{NH})_2\text{C}_4\text{H}_4\text{O}_2$  (m. p.  $256^\circ$ ), is sparingly soluble in hot alcohol. It yields a tetranitro-derivative, which is insoluble in the usual solvents, and decomposes on melting. The dinitro-product forms yellow needles (m. p.  $217^\circ$ ), sparingly soluble in alcohol and chloroform.

When a mixture of naphthylamine and succinic acid is heated at  $190^\circ$  for 12 hours, naphthylsuccinimide and succinnaphthylamide are produced. They are separated by the insolubility of the latter compound in alcohol.

*Naphthylsuccinimide*,  $\text{C}_{10}\text{H}_7\text{N}.\text{C}_4\text{H}_4\text{O}_2$ , forms colourless crystals (m. p.  $152^\circ$ ), soluble in alcohol. It yields a dinitro-derivative (m. p.  $150^\circ$ ). *Succinnaphthylamide*,  $(\text{C}_{10}\text{H}_7.\text{NH})_2\text{C}_4\text{H}_4\text{O}_2$ , is deposited from a solution in strong acetic acid in colourless needles (m. p.  $285^\circ$ ). By the action of strong nitric acid, a mixture of tetra- and octo-nitro-products is

formed. The tetra-nitro-derivative melts at  $225^{\circ}$  with decomposition; it is soluble in strong acetic acid. The octo-derivative melts at  $256^{\circ}$ , and is insoluble in boiling acetic acid. W. C. W.

**Diamidosulphobenzide.** By E. WILD (*Ber.*, **14**, 2184—2185).—This paper is a preliminary notice with regard to the action of methyl alcohol on diamidosulphobenzide in presence of hydrochloric acid. A substituted ammonium chloride is formed of tetramethylsulphobenzide and methyl chloride, which is readily decomposed by heat into these two constituents. V. H. V.

**Polysubstituted Carbamides.** By W. MICHLER and A. ZIMMERMANN (*Ber.*, **14**, 2177—2179).—If a solution of metaphenylenediamine in chloroform is saturated with carbonic chloride, it solidifies after some time with production of a phenylenecarbamide of formula  $C_6H_4<\begin{smallmatrix} NH \\ NH \end{smallmatrix}>CO$ , or some multiple of it. This compound is a white amorphous powder, insoluble in ordinary solvents; it is carbonised at  $300^{\circ}$  without melting.

If a solution of benzidine is treated in the same way, a white amorphous insoluble product is obtained, which cannot, however, be separated from the crude product of the reaction in a sufficiently pure state for exact analysis.

Paramidodimethylaniline and carbonic chloride form a white pulpy mass, which can be purified by dissolving it in hydrochloric acid and precipitating with ammonia. The substituted carbamide formed,  $Me_2N.C_6H_4.NH.CO.NH.C_6H_4.Me$ , crystallises from alcohol in small needles (m. p.  $246^{\circ}$ ). The platinochloride is an orange-coloured precipitate. The compound is identical with a carbamide obtained by Binder (*Abstr.*, 1879, 627). V. H. V.

**Polysubstituted Carbamides.** By W. MICHLER and E. KELLER (*Ber.*, **14**, 2181—2184).—When carbonic chloride is passed into a solution of triphenylguanidine in benzene, a precipitate of the hydrochloride of triphenylguanidine is formed. If this is filtered off and the solution evaporated, colourless tabular crystals (m. p.  $134^{\circ}$ ) of a carbamide,  $PhN:C<\begin{smallmatrix} NPh \\ NPh \end{smallmatrix}>CO$ , separate out. This substance, when heated with hydrochloric acid to high temperatures, is decomposed into aniline and carbonic anhydride; when heated with aniline, it yields carbanilide. On dry distillation, it is completely decomposed into aniline and carbodiphenylimide.

In like manner by the action of carbonic chloride on ethylenediphenyldiamine, a carbamide of composition  $<\begin{smallmatrix} CH_2.NPh \\ CH_2.NPh \end{smallmatrix}>CO$  is formed, which crystallises in large leaflets (m. p.  $209^{\circ}$ ). In order to obtain the chloride corresponding with this amide, the crude product of the action of carbonic chloride on the base is shaken up with water and crystallised from alcohol. A substance (m. p.  $167^{\circ}$ ) was obtained which probably had the constitution  $(COCl.NPh.C_2H_4.NPh)_2CO$ , which is converted very easily into the carbamide (m. p.  $209^{\circ}$ )

described above, and, on dry distillation, is decomposed into carbonic chloride and ethyldiphenylcarbamide.

Also by the action of carbonic chloride on ethylenediparatolyl-diamine, a carbamide,  $\langle \text{CH}_2.\text{NC}_7\text{H}_7 \rangle \text{CO}$ , is obtained, crystallising in large glistening needles (m. p.  $228^\circ$ ); also a chloride (m. p.  $155^\circ$ ), which is easily decomposed into carbonic chloride and ethylene-paraditolylcarbamide. The authors draw attention to this new class of chlorides of carbamides which are thus decomposed into carbonic chloride and the carbamide.

V. H. V.

**Polysubstituted Carbamides.** By F. KAUFMANN (*Ber.*, **14**, 2185).—The author has found that the product of the action of diphenylamine on the chloride of phenylethylcarbamide is identical in chemical and physical properties with the product of the action of ethylaniline on the chloride of diphenylcarbamide. This result is in accordance with the theory of the equality of the carbon-atom affinities, but is in direct contradiction to the results obtained by Schreiner (*Abstr.*, 1881, 88).

V. H. V.

**Action of Phenylthiocarbimide on the Nitranilines.** By S. M. LOSANITSCH (*Ber.*, **14**, 2365).—*Metamononitrodiphenylthiocarbamide* (m. p.  $155^\circ$ ) is deposited in yellow needles from an alcoholic solution containing equal molecules of metanitraniline and phenylthiocarbimide,  $\text{C}_6\text{H}_4(\text{NO}_2).\text{NH}_2 + \text{PhNCS} = \text{NHPh.CS.NH.C}_6\text{H}_4.\text{NO}_2$ . This compound has been previously described by Brückner (*Ber.*, **7**, 1235).

Ortho- and para-nitraniline do not combine with phenylthiocarbimide.

W. C. W.

**Dibromobenzoic Acid from Orthoparadinitrobenzoic Acid.** By W. HALBERSTADT (*Ber.*, **14**, 2215).—Claus and Lade have shown that the action of bromine on orthonitrobenzoic acid gives dibromobenzoic acid and dibromobenzene: the author has obtained similar results with paranitrobenzoic acid. By a similar reaction orthoparadinitrobenzoic acid gives dibromobenzoic acid and bromobenzene. The former compound crystallises in large colourless needles (m. p.  $223^\circ$ ); its barium salt in small coherent crystals of composition  $(\text{C}_7\text{H}_3\text{Br}_2\text{O}_2)_2\text{Ba} + 4\frac{1}{2}\text{H}_2\text{O}$ .

V. H. V.

**Methylphenylamidobenzoic Acid.** By W. MICHLER and A. SARAUW (*Ber.*, **14**, 2180—2181).—If methyldiphenylamine is dissolved in benzene, carbonic chloride passed in to saturation, and the mixture heated in sealed tubes, the acid chloride of methylphenylamidobenzoic acid is formed. On decomposing this with water, dissolving in ammonia, and precipitating with acetic acid, methylphenylamidobenzoic acid is obtained as a reddish precipitate (m. p.  $184^\circ$ ), soluble in hot alcohol. The acid, when heated in sealed tubes with concentrated hydrochloric acid, is decomposed into diphenylamine, carbonic anhydride, and methyl chloride. The barium salt forms glistening leaflets; the silver salt, a white amorphous precipitate.

V. H. V.



**Compounds of Orthobenzoylbenzoic Acid with Phenols.** By H. v. PECHMANN (*Ber.*, **14**, 1859—1867).—By the action of phenols on orthobenzoylbenzoic acid, the author has obtained phthaleïns analogous to the monoxydiphenylphthaleïn already described (*Abstr.*, 1881, 96).

*Phenylresorcinphthaleïn*,  $C_6H_3(OH)_2 \cdot PhC < \overset{\overset{O}{\parallel}}{C_6H_4} > CO$ , is obtained by heating a mixture of 1 mol. resorcinol with 2 mols. benzoylbenzoic acid at 195—200°. This compound (m. p. 175°) dissolves in most solvents; by heating to 200° it is partially decomposed with formation of a substance soluble in alkalis, and giving a green fluorescent liquid. A greenish-blue liquid is obtained by decomposing the phthaleïn with concentrated hydrochloric acid. The *diacetylphthaleïn*,  $C_{20}H_{12}O_4 \cdot 2Ac$ , crystallises in prisms (m. p. 137°). A *dibromo-derivative* is obtained by the action of the necessary quantity of bromine on a solution of the phthaleïn in acetic acid; it forms colourless crystals (m. p. 219°); an excess of bromine decomposes the phthaleïn into benzoylbenzoic acid and tribromoresorcinol.

*Dioxytriphenylmethanecarboxylic acid*,  $C_6H_3(OH)_2 \cdot CHPh \cdot C_6H_4 \cdot COOH$ , obtained by the reduction of the phthaleïn with zinc-dust in the form of glistening crystals (m. p. 184°), is converted into a fluorescent anthranol by the action of concentrated sulphuric acid.

*Phenylresorcinophthaleïn anhydride*,  $C_{20}H_{12}O_7$ , is prepared by heating a mixture of benzoylbenzoic acid and resorcinol with strong sulphuric acid. After suitable purification, this compound forms colourless crystalline needles (m. p. 285°); the diacetyl-derivative is a crystalline body (m. p. 245°). In the course of the preparation of the phthaleïn or its anhydride, a compound was observed characterised by dissolving in alkalis with a red colour and strong green fluorescence, but could not be obtained sufficiently pure for analysis. It probably belongs to the class of complex resorcinol ethers (Barth and Weidel, *Abstr.*, 1878, 61).

*Phenylpyrogallolphthaleïn*,  $C_6H_2(OH)_3 \cdot PhC < \overset{\overset{O}{\parallel}}{C_6H_4} > CO$ , obtained by heating 2 mols. benzoylbenzoic acid with 1 mol. pyrogallol, crystallises from acetic acid solution with 1 mol. of the acid in four-sided tablets (m. p. 189°). The phthaleïn dissolves in alkalis, forming a red-brown, and in hydrochloric acid forming a blue-green solution.

The *triacetyl-derivative*,  $C_{20}H_{11}O_5 \cdot 3Ac$ , crystallises in small delicate needles. Trioxytriphenylmethanecarboxylic acid, formed by reducing the phthaleïn with zinc-dust, is unstable, being converted into an oxyanthranol-derivative.

V. H. V.

**Combination of Orthobenzoylbenzoic Acid with Hydrocarbons.** By H. v. PECHMANN (*Ber.*, **14**, 1865—1867).—By heating benzoylbenzoic acid with acetic anhydride at 100°, a mixed anhydride is formed,  $BzC_6H_4 \cdot COO \cdot Ac$ , in crystalline scales (m. p. 112°). At 200° this compound is decomposed into acetic and benzoylbenzoic anhydrides, the latter of which crystallises in colourless prisms (m. p. 120°). By the action of aluminium chloride on benzoylbenzoic anhydride and benzene, diphenylphthalide is obtained, resembling

in its reactions the substance obtained by Baeyer (Abstr., 1879, 636). The reaction between benzoylbenzoacetic anhydride, benzene, and aluminium chloride, differs from the similar reaction with simple anhydrides of monobasic acids examined by Friedel and Crafts (Abstr., 1878, 792); in the latter a ketonic compound is formed, whilst the former behaves precisely as the free acids. *Phenyltolylphthalide* and *ditolylphthalide* were also prepared, and gave the characteristic oxyanthranol reaction.

V. H. V.

**Metatoluic Acid and its Derivatives.** By O. JACOBSEN (*Ber.*, 14, 2347—2357).—Pure metatoluic acid can be prepared from commercial xylene by the following process:—Pure  $\alpha$ -metaxylenesulphonamide obtained from crystalline metaxylenesulphonic acid is converted into sulphaminetoluic acid by oxidation with potassium permanganate (*Ber.*, 11, 896). The barium salt is prepared from the acid and purified by recrystallisation. The acid is again liberated, and decomposed by the action of strong hydrochloric acid at 230°. The metatoluic acid which is formed is distilled in a current of steam. The acid melts at 110°, and boils at 263°. It is deposited from dilute solutions in slender needles, freely soluble in alcohol and ether. 1 part of the acid dissolves in 1,170 parts of water at 15°, and in 60 at 100°.

*Calcium metatoluate*,  $(C_8H_7O_2)_2Ca + 3H_2O$ , forms silky needles; 100 parts of water at 15° dissolve 3.17 parts, and at 100° 8.2 parts of this salt. *Barium metatoluate*,  $(C_8H_7O_2)_2Ba + 2H_2O$ , crystallises in rhombic plates, and is less soluble than the calcium salt.

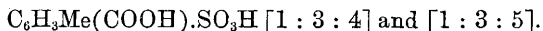
When metatoluic acid is dissolved in bromine, two monobromoderivatives are formed, which can be separated by the difference in solubility of their barium salts.

$\gamma$ -*Bromometatoluic acid*,  $C_8H_7(COOH)MeBr$  [1 : 3 : 4], is deposited from an alcoholic solution in prisms (m. p. 209°). The barium salt crystallises in thin plates or flat prisms containing 4 mols.  $H_2O$ . It is sparingly soluble in water. This acid is identical with the parabromotoluic acid which Ahrens (*Zeits. Chem.*, 1867, 525; 1869, 106) obtained by the oxidation of monobromoxylene.

$\beta$ -*Bromometatoluic acid* (m. p. 140—145°) is probably identical with the acid which Richter obtained by the action of potassium cyanide on bromonitrotoluene. It forms an easily soluble barium salt. On nitration metatoluic acid yields two mononitro-acids, which can be separated by the difference in the solubility of their barium salts.  $\alpha$ -*Nitrometatoluic acid*,  $C_8H_7Me(NO_2).COOH$  [1 : 2 : 3], crystallises in monoclinic prisms (m. p. 219°). Its barium salt contains 2 mols.  $H_2O$ . The amido-acid melts at 172°. The  $\alpha$ -nitro-acid is identical with one of the three acids which Ahrens (*loc. cit.*) obtained by the action of nitric acid on a mixture of toluic acids.

$\beta$ -*Nitrometatoluic acid*,  $C_8H_7Me(NO_2).COOH$  [1 : 4 : 3], is formed in much smaller quantity than the  $\alpha$ -acid. The barium salt is but sparingly soluble in hot water. The free acid melts at 182°. On reduction with tin and hydrochloric acid, it yields an amido-acid (m. p. 132°). On treatment with fuming sulphuric acid metatoluic acid yields two sulphonic acids, which could not be separated from each other. The sodium salt of the mixed acids fused with potash

yields parabromosalicylic acid and symmetrical hydroxytoluic acid. The sulphonic acids produced by the action of fuming sulphuric acid on metatoluic acid must therefore have the formulæ—



W. C. W.

**Oxidation of Parasubstitution-products of Aromatic Hydrocarbons.** By I. REMSEN and L. B. HALL (*Amer. Chem. J.*, **2**, 50).—

*Sulphamine-paratoluic acid*,  $\text{C}_6\text{H}_5\text{NSO}_4 = \text{C}_6\text{H}_3(\text{CH}_3)(\text{SO}_2\text{NH}_2)(\text{COOH})$ , is prepared by gently heating *p*-xylenesulphamide with chromic acid mixture for six or eight hours, washing the crystalline mass which separates on cooling with cold water, then dissolving it in dilute sodium carbonate, evaporating the solution to a small bulk, and leaving it to cool, whereupon any unaltered amide separates out, after which the sulphamine-*p*-toluic acid may be precipitated by hydrochloric acid. It is thus obtained in long needle-shaped crystals melting at 267°. The same acid is obtained by oxidising cymene-sulphonamide with the chromic acid mixture, a compound of the amide with chromic oxide being formed at the same time in green lumps, soluble in alcohol, and reprecipitated therefrom by water.

*Transformation of Sulphamine-p-toluic Acid into the corresponding Hydroxy-acids.*—When this acid is fused in a silver crucible with potash, the melt dissolved in water, and the solution treated with hydrochloric acid, a white crystalline powder is precipitated, which sublimes without melting at a temperature a little above 300°, and forms an aqueous solution which gives a violet-red colour with ferric chloride, by which characters it is shown to consist of hydroxy-terephthalic acid,  $\text{C}_6\text{H}_3(\text{COOH})(\text{OH})(\text{COOH})$  [1 : 2 : 4]; and the mother-liquor, on evaporation to a small bulk, yields another acid, which when purified by boiling with animal charcoal and recrystallisation, forms long transparent shining needles, and yields a lead salt agreeing in character with that of the hydroxy-paratoluic acid,  $\text{C}_6\text{H}_3(\text{CH}_3)(\text{OH})\cdot\text{COOH}$ , prepared by Flesch (*Ber.*, **10**, 144), and by v. Gerichten (*ibid.*, **11**, 1586). The latter chemist, however, assigns to this lead salt 2 mols. water of crystallisation, whereas Remsen and Hall find that it contains only  $1\frac{1}{2}$  mols. water. The acid separated from this salt crystallises in needles, melts at 295°, dissolves with difficulty in cold but easily in hot water, volatilises slowly with water-vapour, and gives no coloration with ferric chloride. These properties show that it is identical with  $\alpha$ -hydroxytoluic acid, in which, as shown by v. Gerichten, the OH-group is in the ortho-position with respect to the methyl-group. Hence it follows that in sulphamine-*p*-toluic acid the sulphonamide-group and the methyl are in the ortho-position with respect to each other, while, as the acid is derived from paraxylene, the methyl and carboxyl are para to one another: hence the formula above given.

The structure of this acid affords a confirmation of a law which is likewise found to hold good in other instances, viz., that the negative group protects the hydrocarbon residue, preventing its oxidation by the chromic acid. A similar protective action is exerted by Cl, Br,  $\text{NO}_2$ ,

and  $\text{SO}_3\text{H}$ : thus when bromine acts upon para-ethyltoluene and the product is oxidised, a bromoparatoluic acid is obtained, the bromine serving to protect the methyl-group from oxidation.

*Sulphoterephthalic acid*,  $\text{C}_8\text{H}_6\text{SO}_7 = \text{C}_6\text{H}_3(\text{SO}_3\text{H})(\text{COOH})_2$ , is produced by heating sulphamine-*p*-toluic acid (1 g.) with potassium permanganate (5 g.) and water (100 c.c.) on the water-bath for seven or eight hours. The solution freed from a slight excess of permanganate by reduction with alcohol, then filtered, concentrated, and treated with hydrochloric acid, yields a white crystalline precipitate of monopotassic sulphoterephthalate,  $\text{C}_6\text{H}_3(\text{COOH})_2(\text{SO}_3\text{K}) + \text{H}_2\text{O}$ , which crystallises from a concentrated aqueous solution in long transparent needles, from a dilute solution in well-developed plates. It is sparingly soluble in cold water, particularly in presence of hydrochloric acid, easily soluble in warm water. H. W.

**The Third Xylic Acid and its Corresponding Xylidenic Acid.** By O. JACOBSEN (*Ber.*, 14, 2110—2116).—By the oxidation of pseudocumene, two only of the three monocarboxylic acids have been obtained. The author has now prepared the third by heating pure monobromoparaxylylene with sodium-amalgam and ethyl chlorocarbonate at  $110^\circ$ , and saponifying the resulting ethereal salt. It is finally purified by distillation with steam, and crystallisation of the calcium salt. *Isoxylic acid*,  $\text{C}_6\text{H}_3\text{Me}_2\text{COOH}$  (1 : 4 : 3), crystallises from alcohol in stellate groups of large needles, free from water (m. p.  $132^\circ$ ; b. p.  $268^\circ$ ), it sublimes below its melting point in long very flexible needles, and distils without decomposition. The *calcium salt*,



is moderately soluble in water. It loses its water at  $150^\circ$ . The paraxylylene obtained by heating this salt with lime, melted without any further purification under  $10^\circ$ . The *barium salt*,  $(\text{C}_9\text{H}_9\text{O}_2)_2\text{Ba} + 4\text{H}_2\text{O}$ , crystallises in compact cakes of very small needles (melting at  $100^\circ$  in its water of crystallisation), which are very soluble. The *potassium salt* crystallises from a syrupy solution in a mass of prisms or needles. The *silver salt* forms a flocculent precipitate, soluble in warm water, and crystallising out again on cooling in small needles. The *copper salt* separates out as a light blue-green amorphous mass which soon changes under the liquid into rosettes of microscopic needles; it is not very soluble in water. The *lead salt* is a white precipitate, moderately soluble in hot water, and is deposited in crystalline flocks on cooling. The *iron salt* is light yellow-brown, and is insoluble in water and ferric chloride. *Isoxylylamide* (m. p.  $186^\circ$ ) is sparingly soluble in water, easily in alcohol. From the latter, it crystallises in masses of fine long soft needles, from the former in beautiful long brittle needles; the acid liberated from the amide by hydrochloric acid melted at  $132^\circ$ .

*Mercury-paraxylyl*,  $(\text{C}_9\text{H}_9)_2\text{Hg}$ , is produced in large quantities as a bye-product in the preparation of isoxylic acid. It is insoluble in water, sparingly soluble in ether and hot alcohol, very easily in chloroform, carbon bisulphide, and the benzene series of hydrocarbons. It separates from toluene in hard, dense, transparent prisms (m. p.  $123^\circ$ ),

which are coloured yellowish by exposure to light. The *dipara-xyllyl*,  $(C_8H_9)_2$ , obtained by distilling this substance, crystallises from hot alcohol in arborescent ramifications of long needles (m. p.  $125^\circ$ ).

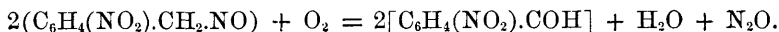
Xylic acid is converted into a dicarboxylic acid,  *$\beta$ -xylidenic acid*, by oxidation with potassium permanganate at ordinary temperatures; the acid is insoluble in cold and only very slightly soluble in hot water, and crystallises in tufts of microscopic needles, thus differing from ordinary xylidenic acid; when a concentrated solution in hydrochloric acid at  $220$ – $230^\circ$  is gradually cooled, it is deposited in small rhombic tablets. It is soluble in hot alcohol, and crystallises out in warts of small needles with a glass-like lustre. It softens at  $310^\circ$  and melts between  $320$ – $330^\circ$ , subliming below its melting point in small dense, vitreous crystals. The *barium salt* does not crystallise, the solution drying up to a gummy mass. The *zinc salt* is easily soluble in cold, but only very sparingly in hot water. The *ammonium salt* is very soluble, and forms a long radiating crystalline mass. The *copper salt* is pale blue. The *silver salt* crystallises from water in nodules of small hard crystals. The ammonium salt gives no precipitate in the cold with zinc sulphate; but when warmed, one forms, if an excess of the zinc salt is avoided. The hydroxy-acid, formed by fusing the sulphonic acid with potash, remains unaltered by heating to  $220$ – $225^\circ$  with hydrochloric acid: it yields a phenol, when distilled with lime. The acid is very soluble in hot, but only very slightly in cold water, crystallising out on cooling in stellate groups of needles (m. p.  $270^\circ$  with slight decomposition). Its aqueous solution gives no reaction with ferric chloride, but solutions of its salts give a pale brown precipitate. From these properties, the author thinks that this acid is a homologue of  $\gamma$ -hydroxyisophthalic acid, and therefore, the  *$\beta$ -xylidenic acid* would be orthoparahomoisophthalic acid, which should be identical with Blomstrand's carboxylic acid made from  $\alpha$ -toluenedisulphonic acid and sodium formate. D. A. L.

**Preparation of Paranitrophenylacetic Acid.** By S. GABRIEL (*Ber.*, **14**, 2341–2342).—*Paranitrophenylacetic acid* can easily be prepared by heating nitrobenzyl cyanide with strong hydrochloric acid at  $100^\circ$  in sealed tubes. Nitrobenzyl cyanide (m. p.  $117^\circ$ ) is obtained by pouring a solution of benzyl cyanide (1 part) in cold fuming nitric acid (9 parts) into 40 parts of cold water. W. C. W.

**Dinitrophenylacetic Acid Derivatives.** By S. GABRIEL and R. MEYER (*Ber.*, **14**, 2332–2341).—*Paradiazonitroso-oxindol chloride*,  $ClN_2.C_6H_3<\frac{CH(NO)}{NH}>CO$ , is deposited in golden needles, when amyl nitrite (10 grams) is added to amidoxindol hydrochloride (4.5 grams), dissolved in a mixture of warm alcohol (100 grams), water (15 grams), and hydrochloric acid (20 grams, sp. gr. 1.13). The solution is allowed to cool before the amyl nitrite is added. Nitroso-oxindol is formed when this diazo-compound is boiled for one hour with alcohol.

*Nitrosomethylorthonitrobenzene* (described *Ber.*, **14**, 826) yields ortho-

nitrobenzaldehyde and nitrous oxide, on oxidation with potassium dichromate, potassium permanganate, or ferric sulphate—



*Methylated nitrosomethylorthonitrobenzene*,  $\text{C}_6\text{H}_4(\text{NO}_2).\text{CHMeNO}$ , is prepared by digesting in sealed tubes at  $100^\circ$ , a mixture of nitrosomethylnitrobenzene (2 parts), with potash (1.2), methyl alcohol (2.5), and methyl iodide (8 parts). After removing the alcohol from the crude product, the residue is distilled in a current of steam. The oily liquid in the distillate solidifies, forming silky needles (m. p.  $58^\circ$ ), which are sparingly soluble in water, but dissolve freely in most of the ordinary solvents. On boiling nitrosomethylnitrobenzene with acetic anhydride, a molecule of water is expelled, and orthonitrobenzonitril,  $\text{C}_6\text{H}_4(\text{NO}_2).\text{CN}$  [1 : 2], is formed. Nitrosomethylnitrobenzene is converted into nitrosomethylamidobenzene by reduction with ammonium sulphide. The amido-derivative crystallises in colourless needles, soluble in alcohol, ether, carbon bisulphide, and glacial acetic acid. The crystals melt at  $132^\circ$ , but begin to sublime at  $100^\circ$ .

By the action of methyl iodide, an atom of hydrogen can be replaced by methyl, forming the compound  $\text{NH}_2.\text{C}_6\text{H}_4.\text{CH.MeNO}$ , which is liquid at the ordinary temperature. The hydrochloride of this base crystallises in thick prisms, and the acetic derivative



in rectangular prisms (m. p.  $109^\circ$ ).

By the action of acetic anhydride on nitrosomethylamidobenzene, a diacetic derivative,  $\text{C}_7\text{H}_5\text{N}_2\text{O}(\text{Ac}_2)$ , is produced, which crystallises in prisms (m. p.  $127.5^\circ$ ), insoluble in acids and alkalis. W. C. W.

**Occurrence of Phenylamidopropionic Acid amongst the Products of Decomposition of Albuminoid Bodies.** By E. SCHULZE and J. BARBIERI (*Ber.*, **14**, 1785—1791).—This acid has been discovered amongst the bodies extracted from the etiolated germinal plants of *Lupinus luteus*; it is separated from the accompanying amido-acids by the insolubility of its copper salt. The free acid, prepared by decomposing the copper salt with sulphuretted hydrogen, crystallises from hot water in shining transparent leaflets. From dilute solutions, it crystallises in groups of white needles containing water of crystallisation. It is sparingly soluble in cold, but easily soluble in hot water, and slightly soluble in alcohol. The formula of this acid is  $\text{C}_9\text{H}_{11}\text{NO}_2$ ; its hydrochloride,  $\text{C}_9\text{H}_{11}\text{NO}_2\text{HCl}$ , crystallises in prisms, unaltered by exposure to the air. By oxidation the acid is converted into benzoic acid; when heated in glass tubes, it melts at about  $250^\circ$ , and is decomposed into a volatile substance, which is apparently the carbonate of a base  $\text{C}_8\text{H}_{11}\text{N}$ . From this carbonate the platinochloride has been obtained having the formula



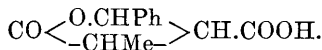
it is soluble in hot water, and on cooling crystallises in yellow leaflets. The base yields benzoic acid on oxidation, and is probably identical with the phenylethylamine  $\text{Ph}(\text{CH}_2)_2.\text{NH}_2$ , described by Bernthsen.

Beside the carbonate of this base, another compound is obtained from the amido-acid, which has not been analysed. The amido-acid distilled with lime appears to yield the base,  $C_8H_{11}N$ , alone.

The authors consider that this phenylamidopropionic acid is a homologue of the phenylamidoacetic acid described by Tiemann, and that this phenylamidopropionic acid owes its formation to the decomposition of albuminoid substances of the seed, during germination; for ungerminated seeds do not yield this acid. Further, by decomposing the albumin of pumpkin seeds with hydrochloric acid and stannous chloride, a small quantity of this phenylamidopropionic acid appears to be formed.

P. P. B.

**Interpretation of Syntheses by Perkin's Reaction.** By R. FITTIG (*Ber.*, **14**, 1824—1826).—In the preparation of phenylisocrotonic acid from benzaldehyde, succinic anhydride and sodium succinate, Jayne (*Annalen*, **208**, 211) has observed the formation of the sodium salt of an acid,  $C_{11}H_{10}O_4$  (m. p.  $100^\circ$ ) which, on heating, is resolved into phenylcrotonic acid and carbonic anhydride. The same products are obtained by substituting acetic anhydride for succinic anhydride; in this case no cinnamic acid is formed. The acid,  $C_{11}H_{10}O_4$ , is monobasic, and, by continued boiling with alkalis or alkaline carbonates, forms a second class of salts having the formula  $C_{11}H_{10}O_5M_2$ . The author, therefore, considers the acid to be a lactonic acid, having the constitution  $CO < \begin{smallmatrix} O.CHPh \\ -CH_2- \end{smallmatrix} > CH.CO.OH$ . A similar acid has also been obtained by Pinfield by the action of benzaldehyde on dry sodium pyrotartrate and acetic anhydride. The acid is the next higher homologue of the above, forming, like it, two classes of salts, and melts at  $177^\circ$ . To it the author assigns the following constitution:—



By dry distillation it is converted into a hydrocarbon,  $C_{10}H_{12}$  (b. p.  $176$ — $177^\circ$ ), which unites with bromine to form a dibromide,  $C_{10}H_{12}Br_2$ . The acid,  $C_{12}H_{12}O_4$ , combines with hydrobromic acid, forming an acid,  $C_{12}H_{13}O_4Br$  (m. p.  $149^\circ$ ), and which, when dissolved in water, is resolved into carbonic anhydride, hydrobromic acid, and an acid,  $C_{11}H_{12}O_2$  (m. p.  $112^\circ$ ).

From these facts the author considers that the reaction takes place between the aldehyde and the sodium salt, and not between the aldehyde and the anhydride, as stated by Perkin. The anhydride is considered to act as a dehydrating agent, otherwise the above compounds would have yielded cinnamic acid. Further, the reaction is attended by a condensation similar to that observed by Würtz in the formation of aldol; and therefore by the action of sodium acetate and benzaldehyde, phenyllactic acid should be obtained: but as this acid is easily converted into cinnamic acid, the latter is obtained as final product, from the manner in which the synthesis is conducted.

P. P. B.

**Notes.** By E. ERLÉNMEYER (*Ber.*, **14**, 1867—1869).—*Bromacrylic Acid.*—The bromacrylic acid from  $\alpha$ - $\beta$ -dibromopropionic acid has the

same crystalline form as the acid from  $\alpha$ -dibromopropionic acid, the potassium salts of the two acids are identical. Hence there is no doubt that  $\alpha$ -bromacrylic acid is formed from both acids.

*Cinnamic Acid Derivatives.*—By allowing a solution of cinnamic acid in acetic acid, saturated with hydrochloric acid, to stand for two years, the author has obtained *phenyl- $\beta$ -chloropropionic acid*, which can be easily recognised by its property of giving styrolene in the cold with sodium carbonate. *Phenyl- $\alpha$ - $\beta$ -dichloropropionic acid*, formed by passing chlorine to saturation into a solution of cinnamic acid in carbon bisulphide, crystallises in white glistening leaflets. With soda solution it gives chlorostyrolene, thus:  $\text{CHPhCl} \cdot \text{CHCl} \cdot \text{COONa} = \text{CHPh} : \text{CHCl} + \text{CO}_2 + \text{NaCl}$ . *Phenylvinylether*,  $\text{CHPh} : \text{CH} \cdot \text{OEt}$ , prepared by heating the chlorostyrolene with sodium ethylate, is a colourless aromatic liquid (b. p.  $217^\circ$ , sp. gr. 0.9812). By heating with water, it yields phenylethylaldehyde and ethyl alcohol. *Paranitrophenylglycidic acid*, formed by the action of hypochlorous acid on sodium paranitrocinnamate, is a crystalline compound; it combines with hydrochloric acid to form paranitrophenyl- $\beta$ -chlorolactic acid.

*Amido- and Amidoiso-capronitril.*—By the action of hydrocyanic acid on isoamylaldehyde-ammonia, amido- and imidoiso-capronitrils are obtained: by a 5 per cent. hydrochloric acid solution, the latter may be separated, after purification, partly in the crystalline state and partly as an oil resembling amidoisovaleronitril in this respect (Abstr., 1881, 85).

*Substituted Guanidines.*—The hydrochloride of the unsymmetrical dimethylguanidine forms large rhombic crystals unaltered in the air; the hydrochloride of the symmetrical dimethylguanidine is very deliquescent. The platinochlorides of both guanidines crystallise in the triclinic system, but they can be distinguished by the ratios of their angles, their optical properties, and their planes of cleavage. The hydrochloride and platinochloride of the unsymmetrical diethylguanidine form clinorhombic crystals. The author has obtained orthotolylguanidine by the action of orthotoluidine hydrochloride on cyanamide.

V. H. V.

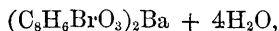
**Derivatives of Mono- and Di-bromanisic Acid.** By P. CRESPI (*Gazzetta*, 1881, 419—429).—1. Monobromanisates.—The sodium and ammonium salts were prepared by saturating the acid (ordinary modification) with sodium carbonate and ammonia respectively; the rest by double decomposition. The *sodium salt*,



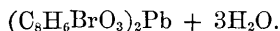
crystallises in long slender needles, very soluble in water, even at ordinary temperatures; only slightly soluble in absolute alcohol, even when heated; more soluble in alcohol of  $95^\circ$  in the cold; very soluble at higher temperatures. The *ammonium salt* decomposes when its aqueous solution is boiled or evaporated over sulphuric acid, depositing bromanisic acid in the form of a crystalline powder made up of small needles. The *silver salt*,  $\text{C}_6\text{H}_3\text{BrO}_3\text{Ag}$ , is a white precipitate, nearly insoluble in cold water, but soluble in boiling water, and separating on cooling in groups of slender anhydrous needles which blacken and decompose at  $100^\circ$ . The *barium salt* is obtained as a



white precipitate which dissolves in boiling water, and crystallises therefrom in fine silky needles having the composition



and giving off the greater part of their water in a vacuum over sulphuric acid. It is nearly insoluble in cold, and only slightly soluble in boiling water; it is not altered by prolonged boiling with baryta-water. The *calcium salt*, likewise obtained by precipitation, separates on cooling from solution in boiling water in fan-shaped groups of long slender needles containing 6 mols.  $\text{H}_2\text{O}$ , part of which is given off over sulphuric acid, and the rest at  $134^\circ$ . The *magnesium salt* separates from hot water in mammellated groups of needles containing 5 mols.  $\text{H}_2\text{O}$ , 4 mols. of which it loses in a vacuum, the fifth at  $160^\circ$ . The *zinc salt* forms slender needles containing  $3\text{H}_2\text{O}$ . The *lead salt* is obtained as a precipitate nearly insoluble in water, even at boiling heat; it crystallises in laminæ having the composition



The *ethylic ether*, prepared by saturating an alcoholic solution of the acid with hydrogen chloride, crystallises in shining needles, slightly soluble in cold, more soluble in hot alcohol and in ether; melting at  $73.5-74^\circ$ .

*Bromanisamide*,  $\text{C}_6\text{H}_5(\text{OMe})\cdot\text{Br}\cdot\text{CONH}_2$ , is prepared by heating the ether with a mixture of 1 vol. aqueous, and 2 vols. alcoholic ammonia at  $130-140^\circ$  in sealed tubes for 24 hours, and precipitating with water; the yield is however but small, as the amide is partly converted by the water present into ammonium bromanisate. It crystallises from alcohol in shining laminæ, from benzene in long slender needles; dissolves sparingly in cold, freely in hot alcohol, also in ether and in benzene; melts at  $185.5^\circ$ .

*Dibromanisic acid*,  $\text{C}_6\text{H}_2\text{Br}_2(\text{OMe})\cdot\text{COOH}$ . This acid, discovered by Reinecke (*Bull. Soc. Chim.* [2], 7, 177), is formed, together with the monobrominated acid, by heating anisic acid suspended in water in a sealed tube at  $120^\circ$ , with rather more than 2 mols. bromine. The crude product is saturated with sodium carbonate mixed with a little caustic soda, and the resulting sodium salts are easily separated by fractional crystallisation, that of the dibrominated acid crystallising out first.

The free acid, obtained by decomposing the sodium salt with hydrochloric acid, separates from alcoholic solution in fine prismatic needles melting at  $213.5-214.5^\circ$ , corr. (at  $207-208^\circ$ , Reinecke). The *sodium salt*,  $\text{C}_6\text{H}_3\text{Br}(\text{OMe})\cdot(\text{COONa})$ , crystallises in needles with 3 mols. water, soluble in alcohol at  $95^\circ$ , and in water. The *ammonium salt* is very unstable. The *silver salt*,  $\text{C}_6\text{H}_5\text{BrO}_3\text{Ag}$ , obtained by precipitation, is very slightly soluble in boiling water, and crystallises in small slender needles. The *barium salt*,  $(\text{C}_6\text{H}_5\text{BrO}_3)_2\text{Ba} + 4\frac{1}{2}\text{H}_2\text{O}$ , prepared by double decomposition, crystallises from boiling water in slender needles, slightly soluble in hot, still less in cold water, insoluble in alcohol and ether. The *calcium salt*, prepared by saturation, is soluble in cold water, and is deposited in light silky crystals containing  $3\frac{1}{2}\text{H}_2\text{O}$ . The *magnesium*, *zinc*, and *lead salts* are white precipitates, insoluble

even in hot water. The *ethylic ether*,  $C_8H_5Br_2O_3 \cdot Et$ , crystallises in shining laminae, soluble in alcohol, insoluble in water, melting at  $88^\circ$  (corr.)  
H. W.

**Hydroxytoluic and Hydroxyphthalic Acids.** By O. JACOBSEN (*Ber.*, 14, 2357—2359).—Symmetrical hydroxytoluic acid is prepared by fusing sodium metatoluenesulphonate with potash. The product is acidified with hydrochloric acid and distilled in a current of steam. The non-volatile residue is heated with hydrochloric acid at  $210^\circ$  for an hour in order to decompose any  $\alpha$ -hydroxyisophthalic acid which may be present, and the unaltered hydroxytoluic acid is extracted from the mixture with ether.

The pure acid crystallises in needles (m. p.  $205^\circ$ ) which are freely soluble in water. Unlike its isomerides, this acid does not volatilise in a current of steam. It can, however, be sublimed. The following salts were prepared:— $Ca(C_8H_7O_3)_2 + 2H_2O$ , transparent prisms, freely soluble;  $Sr(C_8H_7O_3)_2$ , lustrous prisms. The barium and magnesium salts form gum-like masses. Silver, lead, and uranium salts form sparingly soluble crystalline precipitates with this acid. *Methyl hydroxytoluate*,  $C_8H_7O_3Me$ , crystallises in needles and plates (m. p.  $92^\circ$ ) soluble in alcohol and in ether.  
W. C. W.

**Derivatives of  $\alpha$ -Dihydroxybenzoic Acid.** By J. ZEHENTER (*Monatsh. Chem.*, 2, 468—483).—*Sulpho- $\alpha$ -dihydroxybenzoic acid*,  $C_7H_6O_7S + 2H_2O$ , is prepared by heating  $\alpha$ -dihydroxybenzoic acid with 4 to 5 parts of sulphuric acid; it crystallises in needles, dissolves readily in cold water and hot alcohol, yields a deep blood-red coloration with ferric chloride, and a clear red coloration with chloride of lime; it gives white precipitates with both normal and basic lead acetates. The *barium salt*,  $C_7H_4O_7S \cdot Ba + 2H_2O$ , crystallises in prisms; the *hydrogen barium salt*,  $C_{14}H_{10}O_{14}S_2 \cdot Ba + 3H_2O$ , forms a microcrystalline powder. The *potassium salt*,  $C_7H_4O_7K_2 + 3\frac{1}{2}H_2O$ , crystallises in colourless prisms, and is readily soluble in water; the *lead salt*,  $C_7H_4O_7SPb + 2H_2O$ , is obtained from a hot solution in short tetragonal prisms. The *basic copper salt*,  $C_{14}H_6O_{14}S_2Cu_3 + 5H_2O$ , was obtained only as a green crystalline crust. The *silver salt*,  $C_7H_4O_7Ag_2S + 2H_2O$ , is readily soluble in water, and crystallises in brilliant grouped needles.

*Dibrom- $\alpha$ -dihydroxybenzoic acid*,  $C_7H_4O_4Br_2$ , is obtained, together with tribromoresorcinol, by the action of the calculated quantity of bromine on  $\alpha$ -dihydroxybenzoic acid in ethereal solution; it crystallises in colourless needles, is sparingly soluble in cold water, but readily in alcohol and ether. It melts with decomposition at  $214^\circ$ , gives a fine violet coloration with ferric chloride, white precipitates with normal and basic lead acetates, and with silver nitrate. The *potassium salt*,  $C_7H_2O_4Br_2K_2 + 3\frac{1}{2}H_2O$ , crystallises in fine needles; the *calcium salt*,  $C_{14}H_2O_8Br_2Ca + 8\frac{1}{2}H_2O$ , forms crystalline crusts; the *basic lead salt*,  $C_7H_2Br_2O_4Pb$ , is a microcrystalline white powder, insoluble in cold water, and only sparingly soluble in hot water. On boiling a concentrated aqueous solution of dibrom- $\alpha$ -dihydroxybenzoic acid with water, a *dibromoresorcinol* is obtained in long colourless

needles (m. p. 83–85°): it gives a faint violet coloration with ferric chloride, which soon vanishes, a red-brown precipitate appearing after a time; with chloride of lime, it gives an intense yellow coloration. It is readily soluble in alkalis, and is reprecipitated on adding an acid to the solution. This dibromoresorcinol differs both in reaction with ferric chloride and in melting point from that obtained by Hofmann from eosin (*Ber.*, 1875, 64).

*Monobrom- $\alpha$ -dihydroxybenzoic acid*,  $C_7H_5O_4Br + H_2O$ , is prepared in a similar manner to the dibrom-acid: it forms fine prisms, is sparingly soluble in cold water, readily in alcohol and ether. It gives a violet coloration with ferric chloride, and yields white precipitates with basic and normal lead acetates, but not with silver nitrate. The *potassium* salt,  $C_7H_4O_4BrK + 1\frac{1}{2}H_2O$ , crystallises in concentrically grouped needles; the *barium* salt,  $C_{14}H_8O_8Br_2Ba + 7\frac{1}{2}H_2O$ , forms brilliant crystals pretty readily soluble in hot water; the *copper* salt,



is obtained on evaporation in a vacuum in fine tabular crystals; the *lead* salt is obtained as an amorphous precipitate; the *silver* salt,  $C_7H_4O_4BrAg + H_2O$ , is obtained by precipitation from a dilute alcoholic solution as a microcrystalline powder. A. J. G.

**Paratoluyicarboxylic Acid.** By L. ROSER (*Ber.*, 14, 1750—1752).—The amyl salt of this acid has been obtained by an application of the author's method (*Abstr.*, 1881, 31), viz., by the action of amyl chloroxalate on toluene in presence of aluminium chloride.

*Paratoluyicarboxylic acid*,  $C_6H_4Me.CO.COOH$ , is obtained from the amyl salt by decomposing it with hydrochloric acid. It crystallises from light petroleum in large, flat, colourless needles (m. p. about 99°), easily soluble in the ordinary solvents. By oxidation with potassium permanganate, it is converted into paratoluic acid. With benzene and concentrated sulphuric acid it yields reactions similar to those described by Baeyer for isatin (*this Journal*, 36, 937), and by Claisen for phenylglyoxylic acid (*Ber.*, 12, 1505), viz., with these reagents a deep red solution is obtained which changes to a bluish-violet, and on adding water a red powder is thrown down, the alcoholic solution of which imparts a rose colour to silk.

*Barium paratoluyicarboxylate* is precipitated by alcohol from concentrated solutions in fine lustrous needles.

*Silver paratoluyicarboxylate* formed by dissolving silver oxide in the aqueous solution of the acid, is sparingly soluble in cold water, and crystallises from hot water in long colourless needles. It appears probable that ethyl acetate is acted on by amyl chloroxalate in presence of aluminium chloride. The author is still engaged with the study of the products of this reaction. P. P. B.

**Azophenyldiparasulphonic Acid.** By C. LAAR (*Ber.*, 14, 1928—1934).—By the oxidation of potassium sulphanilate, the author has obtained a potassium azophenyldisulphonate (*Abstr.*, 1880, 322), the

acid of which is identical with the  $\alpha$ -azobenzenedisulphonic acid salt of Limpricht (*Ber.*, **14**, 1356).

The *potassium* salt,  $\text{KSO}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3 \cdot \text{K} + 2\frac{1}{2}\text{H}_2\text{O}$ , forms interlaced twin crystals, or small aggregate prisms of an orange or dark red colour: silver nitrate, barium chloride and lead acetate give sparingly soluble crystalline precipitates in aqueous solutions of the salt. By decomposing the silver salt with hydrochloric acid, the *free acid* is obtained in very deliquescent dark orange-red needles or prisms, which cannot be isolated in a state suitable for analysis, for the acid begins to be decomposed even before all the water of crystallisation is given off.

The *sodium* salt forms orange-red scales, the *ammonium* salt rectangular plates. *Azophenylldiparasulphonyl chloride*,  $\text{C}_{12}\text{H}_8\text{N}_2(\text{SO}_2\text{Cl})_2$ , prepared by the action of phosphorus pentachloride on the potassium salt, crystallises in red leaflets (m. p.  $222^\circ$ ), easily soluble in benzene and chloroform. By the action of ammonia on the acid chloride, the amide,  $\text{C}_{12}\text{H}_8\text{N}_2(\text{SO}_2\text{NH}_2)_2$ , is formed, crystallising in orange scales having a silvery lustre; it blackens at  $250^\circ$  without melting. Sulphanilic acid is formed on reducing the potassium salt with stannous chloride. This is contrary to the observations of Limpricht and Moser, who obtained hydrazobenzenedisulphonic acid by the reduction of  $\alpha$ -azobenzenedisulphonic acid (cf. *supra*); Limpricht and others (*Abstr.*, 1878, 722) have also observed that the corresponding dimeta-acid yields a hydrazo-acid on reduction. From the mother-liquors obtained in the preparation of azomonoparasulphonic acid from sulphuric acid and azobenzene, a disulphonic acid may be isolated identical in its properties with the acid described above; the same acid was also prepared by the direct action of sulphuric acid on the monosulphonic acid. The author has succeeded in preparing anhydrous sulphanilic acid, crystallising in tetragonal prisms, and a modification of potassium sulphanilate in compact needles.

V. H. V.

**Hydroxylation by Direct Oxidation.** By R. MEYER and H. BONER (*Ber.*, **14**, 2391—2394).—The potassium salt of  $\alpha$ -metisocymenesulphonic acid (described by Kelbe, *Ber.*, **13**, 1157 and 1399) yields *metahydroxypropylsulphobenzoic acid*,



on oxidation with potassium permanganate. The salts of this acid do not crystallise well. The *barium* and *lead* salts form microscopic crystals which do not contain water of crystallisation.

*Methylmandelic acid*,  $\text{CHPh}(\text{OMe}) \cdot \text{COOH}$ , is prepared by saponifying the ether (b. p.  $248^\circ$ ) which is obtained by acting on sodium methylate with methyl phenylchloracetate. The acid is deposited from light petroleum in tabular crystals (m. p.  $71^\circ$ ). The sodium, barium, and copper salts of this acid crystallise in needles containing 2 mols.  $\text{H}_2\text{O}$ .

Calcium methylmandelate  $(\text{C}_9\text{H}_9\text{O}_3)_2\text{Ca}$ , and silver methylmandelate,  $\text{C}_9\text{H}_9\text{O}_3\text{Ag}$ , crystallise in plates. The methyl salt,  $\text{C}_9\text{H}_9(\text{OMe})\text{O}_2$ , is an oily liquid (b. p.  $246^\circ$ ). On oxidation with potassium permanga-

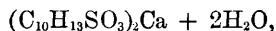
nate, methylmandelic acid yields phenylglyoxylic acid,  $\text{Ph.CO.COOH}$ , instead of a hydroxy-acid.

*Phenylmandelic acid* forms needle-shaped crystals (m. p.  $108^\circ$ ), sparingly soluble in hot water. Sodium phenylmandelate,  $\text{C}_{14}\text{H}_{11}\text{O}_3\text{Na} + 3\text{H}_2\text{O}$ , forms needle-shaped crystals. The copper and silver salts are anhydrous. Phenylmandelic acid is converted into phenylglyoxylic acid by oxidation with potassium permanganate. W. C. W.

**Sulphonic Acids of [1 : 4] Cymene.\*** By A. CLAUS (*Ber.*, **14**, 2139—2144).—By a very careful analysis of the numbers obtained from the salt marked "c," published in Spica's original paper (*Atti del R. Istituto Veneto*, **7**, Serie V, 1881), the author shows that they point not to a mixture of the barium cymenesulphonate (insoluble in alcohol) with the cymenedisulphonate, but to the cymene- $\beta$ -sulphonate with some other substance not in the least connected with the cymene.

The author could not obtain the salt "A" (*loc. cit.*) by sulphonating pure cymene (b. p.  $175^\circ$ ), but as Spica used cymene of b. p.  $178$ — $179^\circ$ , he thinks that its presence (in Spica's experiments) is due to the impurities in the cymene; and as it is soluble to the same extent as the [1 : 3] cymene- $\alpha$ -sulphonate (Claus and Stüsser, this Journal, **38**, 632), suggests that it is this salt.

On treating cymene with sulphuric acid, besides the  $\alpha$ -sulphonic acid, there is always a small quantity of the  $\beta$ -sulphonic acid formed. The latter is found in largest quantities when 1 part of cymene and 5 parts of sulphuric acid are heated on a water-bath and frequently shaken for about six or eight hours. The barium salts of the acids produced are separated, the  $\alpha$ -sulphonate by crystallising out, the disulphonate by extracting the residual mixture with alcohol; the pure  $\beta$ -sulphonate remaining as an amorphous, tenacious, viscous mass, which can be drawn out to threads. It has a intensely sweet taste, whilst the other sulphonate is bitter. When dried over sulphuric acid, it forms a horny mass, which can be rubbed down to a fine powder; heated to  $150^\circ$  it loses 3 mols.  $\text{H}_2\text{O}$ . The formula is  $(\text{C}_{10}\text{H}_{13}\text{SO}_3)_2\text{Ba} + 3\text{H}_2\text{O}$ ; it is soluble in water, from 100 grams of an almost saturated solution 24.75 grams of salt were obtained. Lead [1 : 3] cymene- $\beta$ -sulphonate resembles the barium salt in properties. [1 : 3] cymene- $\beta$ -sulphonic acid is very soluble in water, somewhat less so in alcohol, and insoluble in ether; it separates from the syrupy aqueous solution in granular crystalline aggregations (m. p.  $130$ — $131^\circ$ , uncorr.). The potassium and sodium salts crystallise with 1 mol.  $\text{H}_2\text{O}$ , and are very soluble in water. The copper salt,  $(\text{C}_{10}\text{H}_{13}\text{SO}_3)_2\text{Cu} + \text{H}_2\text{O}$ , crystallises in small green microscopic leaflets. The calcium salt,



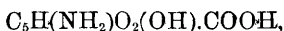
resembles the barium salt. The chloride and amide have as yet only been obtained as non-crystallisable oils. D. A. L.

For previous papers see this Journal, Abstr., 1880, 632, 890, and 1881, 174, 602.

**Comenic Acid.** By T. REIBSTEIN (*J. pr. Chem.* [2], **24**, 276—293).—Comenic acid, prepared and purified by How's method (this Journal [2], **19**, 177), is a monobasic hydroxy-acid, in which there are two hydrogen-atoms replaceable by metals.

*Ethyl comenate*,  $C_5H_2O_2(OH).COOEt$ , prepared by passing hydrochloric acid gas into alcohol in which finely powdered comenic acid is suspended, melts at  $126.5^\circ$ , and not, as How states, at  $135^\circ$ . *Ethylacetyl comenate* (m. p.  $104^\circ$ ) is produced when the ethyl salt is heated with acetic anhydride at  $150^\circ$ . It is decomposed by water, and gives no coloration with ferric chloride.

Nitric and nitrous acids decompose comenic acid if water is present, oxalic and hydrocyanic acids being produced. *Ethyl nitrocomenate*,  $C_5H(NO_2)O_2(OH).COOEt$ , is formed when ethyl comenate is suspended in anhydrous ether, and treated with nitrous acid. It forms small yellow needles (m. p.  $147^\circ$ ); its aqueous solution is coloured red by ferric chloride, and it forms metallic salts, of which the sodium, silver, and barium salts explode when heated. When the nitro-compound is reduced by tin and hydrochloric acid, the amido-acid,

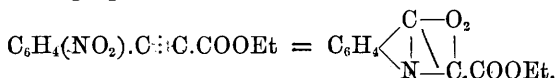


crystallising with 1 mol.  $H_2O$ , is formed, and this produces an indigo-blue coloration with ferric chloride. Amidocomenic acid hydrochloride contains 3 mols.  $H_2O$ , and is decomposed at  $110^\circ$ . If ammonia is passed into an ethereal solution of comenic acid, the ammonia salt is produced, which, treated with hydrochloric acid, is converted into comenamide,  $C_5H_2O_2(OH).CONH_2$ , isomeric with comenamic acid. The potassium salt loses its molecule of crystalline water, and is also decomposed at  $100^\circ$ . *Ethyl comenamate*, prepared according to How's method, crystallises with 1 mol.  $H_2O$  and melts at  $205^\circ$ ; the barium salt  $[C_5H(NH_2)O(COOEt)O]_2Ba + 2H_2O$ , is readily dissolved by hot water, but is soon decomposed into barium comenate, from which the free acid can easily be obtained. When bromocomenic acid is heated with ammonia at  $150^\circ$ , a black fluid is formed, in which the ammonium comenamate is dissolved. By carefully acidifying the solution a precipitate of comenamic acid is obtained.

*Hydroxycomenic acid*,  $C_5HO_2(OH_2).COOH + H_2O$ , is produced when barium bromocomenete is boiled for a long time with excess of baryta-water; the acid crystallises in long needles with 3 mols.  $H_2O$ , or in short prisms, with 1 mol.  $H_2O$ . A small amount of ferric chloride added to the aqueous solution produces a blue, and a large quantity a red coloration. The ethyl salt melts at  $204^\circ$ . *Ethyl diacetoxycomenate* is easily obtained by the action of acetic anhydride on ethyl hydroxycomenate at  $150^\circ$ ; it melts at  $75^\circ$ , and is slowly decomposed by water. The ammonium, barium, and potassium salts of hydroxycomenic acid have been prepared. Hydroxycomenamic acid has been prepared by a process similar to that employed for the preparation of comenamic acid; it crystallises in small white well-defined needles, and is isomeric with amidocomenic acid. On adding barium chloride to its aqueous solutions, or potash to alcoholic solution, a blue precipitate is obtained. *Hydroxycomenamic acid*,  $C_5H_2NO(OH_2)_2.COOH$ , in all probability bears the same relationship to pyromecazonic acid,

$C_5H_3NO(OH)_2$ , that comenamic acid bears to pyromeconic acid,  $C_5H_3O_2OH$ . Unsatisfactory results were obtained when hydriodic acid was allowed to act on comenic acid, the acid being completely decomposed with formation of oxalic acid. E. W. P.

**Compounds of the Indigo-group.** By A. BAEYER (*Ber.*, **14**, 1741—1746).—*Ethyl isatogenate*. This compound is obtained by the action of concentrated sulphuric acid on ethyl orthonitropropiolate; it crystallises in yellow needles, m. p.  $115^\circ$ . Its formation is expressed by the following equation:—



Isatogenic acid is very unstable, and cannot be obtained either from the above salt, or from free orthonitropropionic acid, as it is immediately converted into isatin.

*Indoïn*,  $C_{32}H_{20}N_4O_5$ , is obtained by treating a solution of orthonitropropionic acid with a reducing agent (*e.g.*, ferrous sulphate). It resembles indigo, but differs in its solubility in cold sulphuric acid, forming a blue solution; also in being soluble in cold aniline and in aqueous sulphurous acid.

*Indoxyl-compounds*.—*Ethyl indoxylate*,  $C_{11}H_{11}NO_3$ , obtained by reducing nitropropionic acid with ammonium sulphide, crystallises in thick prisms (m. p.  $120-121^\circ$ ). It contains a hydroxyl group, and has the character of a phenol. Its acetic derivative crystallises in white needles (m. p.  $138^\circ$ ). From its sodium or potassium salt the ethyl salt has been obtained, crystallising in large colourless crystals (m. p.  $98^\circ$ ). Ethyl indoxylate is converted into indigo by heat, and into indigo-sulphonic acid by the action of strong sulphuric acid. *Indoxylic acid*,  $C_9H_7NO_3$ , has been prepared from the ethyl salt, m. p.  $122-123^\circ$ ; on exposing an alkaline solution of it to the air, indigo is formed. *Ethyl-indoxylic acid*,  $C_{11}H_{11}NO_3$ , is obtained from the ethyl derivative of ethyl indoxylate; it crystallises from alcohol in leaflets, m. p.  $160^\circ$ . Its alkaline solutions do not yield indigo, but indigo is obtained by treating it with ferric chloride and hydrochloric acid.

*Nitrosoethyl indoxylate*,  $C_{11}H_{10}(NO)NO_3$ , is obtained by the action of nitrous acid on ethyl indoxylate; it crystallises in large flat golden-yellow needles. This compound behaves like nitroso-oxindol; it forms an amido-derivative, which by ferric chloride and hydrochloric acid is converted into isatin. To indoxylic acid the author attributes the fol-

lowing constitution:— $C_6H_4 \begin{array}{c} \diagup C(OH) \\ | \quad \diagdown \\ N- \end{array} CH.COOH$ . Its ethyl salt is

formed by replacing the hydrogen in the carboxyl group by ethyl, and the ethyl derivative by replacement of the hydrogen in the hydroxyl group attached to the single carbon-atom.

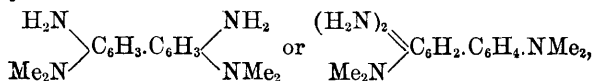
*Indoxyl*,  $C_6H_4 \begin{array}{c} \diagup C(OH) \\ | \quad \diagdown \\ N- \end{array} CH_2$ , is formed by heating indoxylic acid

above its melting point, when it is decomposed with evolution of carbonic anhydride and formation of indoxyl. The same decomposition is produced by boiling the aqueous solution of indoxylic acid. Indoxyl is a brown oil, volatile in steam, and imparts a blue fluorescence to water. It has both acid and basic properties, and like indoxylic acid is converted into indigo by oxidation. Indoxyl and orthonitropropionic acid yield indoin, moreover, indoxyl or indoxylic acid dissolved in sodium carbonate yields indigo when acted upon by nitropropionic acid. Indirubin is obtained by the action of isatin on indoxyl, and the bromo-derivative,  $C_{15}H_9BrN_2O_2$ , when bromisatin is substituted for isatin. *Ethylindoxyl*,  $C_8H_6(Et)NO$ , is obtained from ethylindoxylic acid, just as indoxyl is obtained from indoxylic acid. It is a colourless oil, of an odour resembling indol, and forms a crystalline compound with picric acid. It is converted into isatin and indigo in the same way that ethylindoxylic acid is.

*Potassium indoxylsulphonate* is obtained by the action of potassium hydrogen sulphate on indoxyl; it is identical with that prepared by Baumann and Brieger (*Zeits. Phys. Chem.*, **3**, 254), and therefore the indoxyl formed in urine is identical with that prepared synthetically. The oil obtained by the above authors (*loc. cit.*), and also by Baumann and Tiemann (this Journal, **36**, 806, 935), by treating the potassium indoxylsulphonate with hydrochloric acid, is indoxyl. P. P. B.

### Substituted Derivatives of Benzidine and Diamidoditolyl.

By W. MICHLER and S. PATTINSON (*Ber.*, **14**, 2161—2167).—By heating dimethylaniline with about three times its weight of concentrated sulphuric acid at  $180-210^\circ$ , water and sulphurous acid are given off, and tetramethylbenzidine is formed. This change may be explained thus: at first dimethylanilinesulphonic acid is formed, which reacts with a further quantity of dimethylaniline, according to the equation,  $SO_3H.C_6H_4.NMe_2 + PhNMe_2 = H_2O + SO_2 + Me_2N.C_6H_4.C_6H_4.NMe_2$ . The crude product of the reaction is distilled in a current of steam to separate the unattacked dimethylaniline, and tetramethylbenzidine is left as a flocculent mass, which, after suitable purification, is obtained in colourless crystals (m. p.  $195^\circ$ ), sparingly soluble in cold alcohol and ether, easily soluble in hot alcohol. Tetramethylbenzidine is a biacidic base, and forms di-haloid salts, crystallising in white needles. The same base may also be obtained by the oxidation of dimethylaniline with lead peroxide, but the yield is small. On dissolving benzidine in methyl alcohol, and heating it with methyl iodide in sealed tubes, a tetrammonium iodide of formula  $Me_2N.C_6H_4.C_6H_4.NMe_2I$  is obtained, crystallising in white needles (m. p.  $263^\circ$ ). The corresponding chloride forms white, and the platinochloride golden-coloured crystals. On distilling the tetra-ammonium iodide with soda-lime, it is decomposed into tetramethylbenzidine and methyl iodide. The action of sodium nitrite on tetramethylbenzidine gives rise to a dinitro-derivative, which on reduction with tin and hydrochloric acid, yields diamido-tetramethylbenzidine,





which crystallises in white leaflets (m. p.  $168^{\circ}$ ). The hydroiodide and hydrochloride of this base crystallise in needles, sparingly soluble in water; the platinochloride is a golden powder. By a reaction similar to that described above, a tetrethylbenzidine is obtained, crystallising in white needles (m. p.  $85^{\circ}$ ), and identical with the tetrethylbenzidine prepared directly by P. W. Hofmann from benzidine.

By a similar process tetramethyldiamidoditolyl is obtained from dimethylparatoluidine; this base crystallises in white needles, insoluble in water, soluble in alcohol and ether; its composition is expressed by the formula  $\text{Me}_2\text{N} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NMe}_2$ . V. H. V.

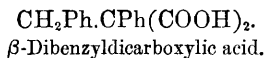
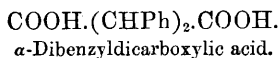
**Two Isomeric Dibenzylldicarboxylic Acids.** By C. L. REIMER (*Ber.*, 14, 1802—1808).—These isomeric acids are obtained by reducing an alcoholic solution of stilbenedicarboxylic anhydride with sodium-amalgam, and are separated by the difference in solubility of their barium salts.

*$\alpha$ -Dibenzylldicarboxylic acid*, which is obtained from the less soluble barium salt, crystallises from water in thick prisms containing 2 mols.  $\text{H}_2\text{O}$ ; the crystals melt at  $183^{\circ}$ , and after the water is expelled it solidifies to melt again at  $222^{\circ}$ . This acid is identical with that described by Franchimont (*Ber.*, 5, 1048). Its salts are all sparingly soluble in water. The ethyl salt,  $\text{C}_{14}\text{H}_{12}(\text{COOEt})_2$ , crystallises in silvery needles (m. p.  $84$ — $85^{\circ}$ ). A dinitro-derivative,  $\text{C}_{16}\text{H}_{12}\text{O}_4(\text{NO}_2)_2$ , has been prepared; it is soluble in hot water, alcohol, and acetic acid, and is described as a resinous solid: dried over sulphuric acid, it retains 1 mol.  $\text{H}_2\text{O}$ , which it loses at  $100$ — $150^{\circ}$ , and when anhydrous melts at  $226^{\circ}$ .

*$\beta$ -Dibenzylldicarboxylic acid* is obtained from the more soluble barium salt. It crystallises from alcohol in small needles (m. p.  $229^{\circ}$ ), which are insoluble in water, and only sparingly soluble in benzene or glacial acetic acid. Its salts are more soluble than those of its isomeride. The ethyl salt forms small needles (m. p.  $136^{\circ}$ ), easily soluble in hot, less soluble in cold alcohol. The dinitro-derivative (m. p.  $242^{\circ}$ ) is insoluble in water, and sparingly soluble in alcohol.

These isomerides may be converted into one another, the  $\alpha$ -acid when heated with hydrochloric acid forming the  $\beta$ -acid, and the latter when heated with baryta-water being reconverted into the  $\alpha$ -acid. Both acids when distilled with lime yield distilbene and dibenzyl, and are both oxidised with difficulty by potassium permanganate or chromic mixture. Both acids when heated with strong sulphuric acid lose 2 mols.  $\text{H}_2\text{O}$ , forming dibenzylldicarbonide,  $(\text{C}_{16}\text{H}_{10}\text{O}_2)$ , m. p.  $202^{\circ}$ .

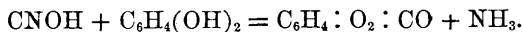
The constitution of the dibenzylldicarboxylic acids is represented by the following formulæ:—



P. P. B.

**A Phenylenecarboxylic Ether.** By K. BIRNBAUM and G. LURIE (*Ber.*, 14, 1753—1755).—A compound having the composition  $\text{C}_7\text{H}_4\text{O}_3$  is obtained by heating resorcinol, cyanuric acid, and zinc chloride

together at 200°. This compound is insoluble in water; it dissolves in alcohol with a red colour, and is precipitated by water from its alcoholic solutions as a red powder. It dissolves in alkalis, forming a green fluorescent solution, the fluorescence being destroyed by acids. When dissolved in glacial acetic acid and treated with bromine, it yields a compound having the formula  $C_7Br_4O_3$ . This compound is also obtained by acting on resorcinol with carbonyl dichloride, and hence its constitutional formula is  $C_6H_4<\overset{O}{\underset{O}{\text{C}}}>CO$ . Its formation from cyanuric acid is explained by supposing the cyanuric acid to be decomposed into cyanic acid, and then the following reaction to take place:—



Not only was an evolution of ammonia observed during the reaction, but it was also found in the product of the reaction. It is also probable that some of the cyanuric acid is decomposed into ammonia and carbonic anhydride by the water combined with it as water of crystallisation, or the water in the zinc chloride. The carbonic anhydride thus formed reacts with the resorcinol to form the phenylene-carbonic ether and water.

P. P. B.

**Preparation of Paramidostyrene and Paracoumaric Acid from Paranitrocinnamic Acid.** By G. BENDER (*Ber.*, **14**, 2359—2361).—When ethyl paranitrocinnamate is reduced with tin and hydrochloric acid, paramidocinnamic acid and paramidostyrene,  $C_6H_4(NH_2).C_2H_3$ , are produced. The latter is insoluble in alkalis, but dissolves in alcohol and in ether.

Attempts to convert paramidocinnamic acid into paracoumaric acid were unsuccessful.

W. C. W.

**Carbostyryl.** By P. FRIEDLÄNDER and H. OSTERMAIER (*Ber.*, **14**, 1916—1921).—The authors allude to the interest attached to carbostyryl and its derivatives from their intimate connection with quinoline. Carbostyryl is best prepared by the reduction of ethyl orthonitrocinnamate by ammonium sulphide in alcoholic solution; quantities of oxycarbostyryl are formed at the same time, varying with the conditions of the reaction. Pure *carbostyryl* melts at 198—199° (*Abstr.*, 1881, 171); with the alkalis and alkaline earths it forms crystalline salts, which are decomposed by carbonic acid. *Ethyl-carbostyryl*,  $C_9H_8NOEt$ , is obtained by the action of ethyl iodide on the potassium salt of carbostyryl, and can be separated from the crude product by distillation in a current of steam. It is a colourless, thick oil, boiling at 250° with slight decomposition, and has basic properties, dissolving in mineral acids with formation of deliquescent salts; with platonic chloride, it gives a soluble crystalline platinochloride, and with potassium ferrocyanide a sparingly soluble crystalline precipitate of ethyl-carbostyryl ferrocyanide. *Oxycarbostyryl*,  $C_9H_7NO_2$ , prepared by the process mentioned above, resembles carbostyryl in its properties; it melts at 190°, and sublimes in delicate needles. It is a strong monobasic acid and decomposes the carbonates. The salts of the alkali-metals

are readily soluble, but the salts of the heavy metals are insoluble precipitates. A characteristic test for oxycarbostyryl is the deep red colour formed when its aqueous solution is heated with nitric acid. On heating carbostyryl with baryta a strong odour of indol is noticeable.

*Ethylloxycarbostyryl*,  $C_9H_6EtNO_2$ , prepared by the action of ethyl iodide on the potassium salt of oxycarbostyryl, forms long thick prisms (m. p.  $73^\circ$ ), insoluble in water, soluble in most other menstrua. Ethylloxycarbostyryl, like ethylcarbostyryl, acts as a strong base, forming crystalline hygroscopic precipitates with mineral acids. Oxycarbostyryl is easily oxidised by alkaline permanganate, forming ortho-nitrobenzoic acid; carbostyryl under the same conditions gives a substance resembling isatin in its characteristic reactions.

V. H. V.

**Some New Aromatic Hydrocarbons.** By G. GOLDSCHMIDT (*Monatsh. Chem.*, **2**, 432—447).—The author has applied Zincke's method for the synthesis of hydrocarbons (heating benzyl chloride with an aromatic hydrocarbon and powdered zinc) to the higher series of aromatic hydrocarbons, the only previous result in this direction being the synthesis of benzyl-naphthalene by Frote (*Compt. rend.*, **76**, 639; this Journal, 1873, 891).

*Parabenzyl-diphenyl*,  $CH_2Ph.C_6H_4Ph$ , is prepared, together with isobenzyl-diphenyl by heating diphenyl, benzyl chloride, and zinc at  $100^\circ$ . It crystallises from alcohol in plates, and from hot glacial acetic acid in flat needles; it is readily soluble in alcohol and ether, melts at  $85^\circ$ , and boils at  $285$ — $286^\circ$  in a vacuum. On oxidation with chromic acid in glacial acetic acid, it yields *paraphenylbenzophenone*,  $C_6H_5.CO.C_6H_4Ph$ , which crystallises in fine colourless scales, melts at  $104^\circ$ , is readily soluble in alcohol, and is reduced to the parent hydrocarbon by nascent hydrogen. On oxidation, this ketone is converted into benzoyl-benzoic acid, in which the benzoyl and carbonyl-groups are known to be in the para-position.

*Isobenzyl-diphenyl*,  $C_{19}H_{16}$ , obtained as above is more readily soluble in all solvents than its isomeride, and often exhibits the phenomenon of surfusion on separating from solution. It crystallises in monosymmetrical needles, melts at  $54^\circ$ , and boils at  $283$ — $287^\circ$  in a vacuum. As it is completely burnt to carbonic anhydride and water, on oxidation it is probably an ortho-compound.

*Benzylfluorene*,  $CH_2Ph.C_6H_4$   
 $\begin{array}{c} | \\ C_6H_4 \end{array} \rangle CH_2$ , is prepared by heating fluorene,

zinc, and benzyl chloride; it crystallises in white plates (m. p.  $202^\circ$ ). The small amount obtained precluded further examination.

*Benzylphenanthrene*,  $C_{21}H_{16}$ , crystallises in brilliant needles, (m. p.  $155$ — $156^\circ$ ), sparingly soluble in alcohol, more readily in benzene. On oxidation, it yields benzoic acid and phenanthraquinone.

On heating stilbene and benzyl chloride with zinc, the only crystalline product obtained was anthracene. A. J. G.

**Purification of Naphthalene.** By G. LUNGE (*Ber.*, **14**, 1754—1757).—The author recommends the following method of purification.

The crude naphthalene is stirred up with 5 to 10 per cent. of its weight of sulphuric acid (sp. gr. 66°); to this is added gradually finely-powdered manganese dioxide or dried Weldon-mud, amounting to about 5 per cent. of the weight of naphthalene, and then the whole is heated on a water-bath until the action ceases. When cold the cake of naphthalene is removed and repeatedly melted under water, then under water containing a little soda, and finally under water again. The naphthalene obtained in this way and subsequently distilled remained perfectly white for eight or nine months.

P. P. B.

**Action of Bromine on Naphthalene.** By G. MAGATTI (*Gazzetta*, 1881, 357—359).—Laurent, by treating naphthalene with bromine, obtained a mono- and a di-bromonaphthalene. Glaser, several years afterwards, by acting on 1 mol. naphthalene with 2 mols. bromine, obtained two dibromonaphthalenes, one (identical with that of Laurent) melting at 81°, the other at 76°. Jolin also obtained two dibromoderivatives, viz., that of Laurent, and another melting at 60·5—61°. Guareschi about the same time confirmed Glaser's results, but observed that the compound melting at 76° has, when impure, a lower melting point, viz., 71°, a result which so far confirms that of Jolin as to indicate the existence of a dibromonaphthalene melting below 76°.

To throw further light on these compounds, the author of the present paper added bromine (750 g.) drop by drop to naphthalene (300 g.), contained in a large flask surrounded by cold water, and, after the evolution of hydrogen bromide had ceased, treated the product with boiling alcohol, which dissolved a brown oil (probably monobromonaphthalene, b. p. 285°), leaving a residue which dissolved in ordinary alcohol at boiling heat, the solution, while still warm, depositing crystals which, after two recrystallisations, melted exactly at 81°. The mother-liquors yielded a small additional quantity of the same compound, and when further concentrated and left to cool, deposited crystalline masses, which began to melt at 67°, but were not entirely fused till the temperature was raised to 90°. This substance exhibited nearly the same properties even after repeated crystallisation from alcohol; but on dissolving it in glacial acetic acid, and leaving the solution to cool, white scales were deposited, which, after several recrystallisations, melted constantly at 120°. The substance thus obtained is a dibromonaphthalene, very readily soluble in ether, moderately soluble in alcohol, sparingly in glacial acetic acid; it is identical with that which Jolin obtained by the action of phosphorus pentabromide on  $\alpha$ -dinitronaphthalene, and apparently also with that which Darmstädter u. Wichelhaus prepared by the action of bromine on  $\alpha$ -naphthalenesulphonic acid.

After the removal of this modification (designated as  $\gamma$ ), the acetic solution deposited, on concentration, mammellated groups of needles, (m. p. 67—76°), apparently consisting of a mixture of two, and possibly a greater number of dibromonaphthalenes.

H. W.

**Preparation of  $\alpha$ -Naphthaquinone.** By C. LIEBERMANN (*Ber.*, 14, 1795—1796).—In a former communication (*Ber.*, 14, 1315) the author has described a method for preparing  $\beta$ -naphthaquinone from

$\beta$ -naphthol-orange. The isomeride of this latter compound, viz.,  $\alpha$ -naphthol-orange, which is the sodium salt of the benzenesulphonic acid of azo- $\alpha$ -naphthol,  $\text{SO}_3\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_5\text{OH}$ , may in a similar manner be converted into  $\alpha$ -naphthaquinone. The yield of  $\alpha$ -naphthaquinone is about 40 per cent. of the theoretical quantity.

P. P. B.

**Constitution of  $\beta$ -Naphthaquinone.** By P. JACOBSEN (*Ber.*, **14**, 1791—1795).— $\beta$ -Naphthaquinone may be obtained from nitro- $\beta$ -acetanaphthalide. In order to determine the constitution of  $\beta$ -naphthaquinone, the author has converted nitro- $\beta$ -acetanaphthalide into nitro- $\beta$ -naphthylamine by acting on the former with alcoholic potash. By the diazo-reaction, the latter compound yields  $\alpha$ -nitronaphthalene, thus showing that the nitro- $\beta$ -acetanaphthalidie contains the nitro-group in the  $\alpha$ -position. Further, since phthalic acid is obtained by oxidising  $\beta$ -naphthaquinone, it is evident that the nitro- and amido-groups contained are in the same benzene nucleus. Hence the constitution of nitro- $\beta$ -acetanaphthalide may be expressed by the formula (I)  $\text{NHAc} : \text{NO}_2 = [3 : 4]$ , or (II)  $\text{NO}_2 : \text{NHAc} = [1 : 3]$ . If the formula I be correct, then this compound on reduction would yield an anhydro-base. The author has reduced nitro- $\beta$ -acetanaphthalide, and has obtained the hydrochloride of ethenyl- $\alpha$ - $\beta$ -naphthylenediamine,

$\text{C}_{10}\text{H}_6 \begin{array}{c} \diagup \text{N} \\ \diagdown \text{N} \end{array} \text{CMe, HCl}$ , thus proving the correctness of the formula I.

Hence  $\beta$ -naphthaquinone will probably have the constitution assigned to it by Liebermann, viz., that of an  $\alpha$ - $\beta$ -ortho-derivative  $\text{O} : \text{O} = [1 : 2]$ .

P. P. B.

**$\alpha$ -Naphthaquinoneanilide and its Derivatives.** By C. BALTZER (*Ber.*, **14**, 1899—1905).—The author at the outset alludes to the constitutional formula proposed by Plimpton for the aniline derivative of naphthaquinone (this Journal, Trans., 1880, 636). The more recent researches of Zincke and Wülping on thymoquinone and of Plimpton himself have shown that the amine-grouping takes the place of a hydrogen-atom, and the oxygen-atom affinities remain unaltered (*Ber.*, **14**, 92). Therefore, the third formula proposed by Plimpton,  $\text{NHPh} \cdot \text{C}_{10}\text{H}_5\text{O}_2$ , is the more probable.  $\alpha$ -Naphthaquinoneanilide behaves as thymoquinone in yielding hydroxynaphthaquinone and aniline on boiling with acids or alkalis. The ethoxynaphthaquinone,  $\text{C}_{10}\text{H}_3 \cdot \text{O}_2 \cdot \text{OEt}$ , prepared from the silver salt and ethyl bromide, crystallises in long golden needles (m. p.  $126^\circ$ ). By the action of bromine on naphthaquinoneanilide, a dibromo-derivative is obtained, which crystallises in deep-red needles (m. p.  $238$ — $240^\circ$ ). On boiling the dibromo-derivative with dilute alkalis, it is converted into parabromaniline and a bromoxyquinone (identical with that obtained by Merz and Diehl, *Abstr.*, 1878, 736). This shows that the dibromnaphthaquinoneanilide has the constitution,  $\text{C}_6\text{H}_4\text{Br} \cdot \text{C}_{10}\text{H}_4\text{BrO}_2$ .

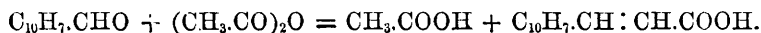
Dibromonaphthaquinoneanilide, when heated for a long time with concentrated alcoholic potash, gives a monobromo-derivative,  $\text{C}_6\text{H}_4\text{Br} \cdot \text{NHC}_{10}\text{H}_5\text{O}_2$ , in red needles (m. p.  $266$ — $269^\circ$ ), which readily decompose into parabromaniline and hydroxyquinone. The same monobromonaphthaquinoneanilide is produced by the action of para-

bromaniline and hydroxyquinone, but bromoxyquinone and aniline yield an isomeride,  $\text{NHPh.C}_{10}\text{H}_7\text{BrO}_2$ , crystallising in ruby-red four- or eight-sided prisms (m. p.  $165^\circ$ ).

By dissolving naphthaquinoneanilide in nitric acid, a monitro-derivative,  $\text{NH}(\text{C}_6\text{H}_4\text{NO}_2).\text{C}_{10}\text{H}_5\text{O}_2$ , is obtained in red needles, which do not melt even at  $270^\circ$ . It can be decomposed by alcoholic sulphuric acid into hydroxynaphthaquinone and paranitraniline, from which it can again be built up by boiling for some time in alcoholic solution. By reduction of the nitro-derivative, phenylenediamine-naphthaquinone,  $\text{NH}(\text{C}_6\text{H}_4\text{NH}_2).\text{C}_{10}\text{H}_5\text{O}_2$ , is obtained in blackish needles (m. p.  $175\text{--}177^\circ$ ).  
V. H. V.

**Dihydroxynaphthalene.** By A. WEBER (*Ber.*, **14**, 2206—2210).—In the first portion of this paper, the author gives an account of the best method of preparation of dihydroxynaphthalene from the crude calcium salt of naphthalenedisulphonic acid, obtained by the process of Ebert and Mertz from naphthalene and concentrated sulphuric acid (*Ber.*, **4**, 609; comp. also Armstrong and Graham, *Trans.*, 1881, 139). It appears that the best yield (95 per cent. of that required by theory) was obtained when not too large quantities of the calcium salt were fused with soda in an atmosphere of hydrogen. Dihydroxynaphthalene shrivels up and becomes dark when heated in the air to  $170^\circ$ , and melts at  $184^\circ$ . On working in an atmosphere of hydrogen, it melts at  $184^\circ$ , remaining white throughout the operation. On heating dihydroxynaphthalene with concentrated sulphuric acid at  $120^\circ$ , a sulphonic acid is formed. At a rather higher temperature ( $160\text{--}180^\circ$ ) sulphurous anhydride is given off and a dark mass is left. This dissolves in alkalis with formation of a cherry-red solution, from which acids precipitate a red flocculent substance, capable of dyeing silks and wools. A similar dye-stuff is obtained when dihydroxynaphthalene is heated with zinc chloride or concentrated hydrochloric acid. It is probable that the constitution of this substance is analogous to the complex resorcinol ethers obtained by Barth (*Abstr.*, 1878, 61). *Dimethoxynaphthalene*,  $\text{C}_{10}\text{H}_8(\text{OMe})_2$ , prepared by heating a mixture of dihydroxynaphthalene, methyl iodide, potash, and methyl alcohol, forms white leaflets (m. p.  $134^\circ$ ). The *diacetyl-derivative*,  $\text{C}_{10}\text{H}_6(\text{OAc})_2$ , from dihydroxynaphthalene and acetic chloride, forms glistening leaflets (m. p.  $129^\circ$ ), and the *dibenzoyl-derivative*,  $\text{C}_{10}\text{H}_6(\text{OBr})_2$ , prepared by a similar process, crystallises in leaflets (m. p.  $138\text{--}139^\circ$ ), soluble in alcohol.  
V. H. V.

**Synthesis of Naphthylacrylic Acid.** By F. LUGLI (*Gazzetta*, 1881, 393—396).—The action of an organic anhydride mixed with a sodium salt on an aromatic aldehyde (Perkin's reaction), which has already led to the synthesis of cinnamic (phenyl-acrylic) acid, and several of its analogues, has been applied by the author to the formation of naphthylacrylic acid, namely, by the action of acetic anhydride mixed with sodium acetate on naphthaldehyde, according to the equation:



The aldehyde, prepared by heating a mixture of naphthoate and formate of calcium, was heated for about 10 hours at  $160-180^{\circ}$  with half its weight of sodium acetate and 10 times its weight of acetic anhydride, till the liquid on cooling solidified to a yellow homogeneous mass of the new acid, which, after purification by a process for which we must refer to the original paper, was obtained in the form of a white mass having a nacreous lustre. It is very slightly soluble in cold, much more freely in boiling water, dissolves also in alcohol, very readily in ether, and separates from the alcoholic solution in a mass of needle-shaped crystals. It melts, without decomposition, at  $205-207^{\circ}$ , and is but slightly volatile. The silver salt is white and somewhat altered by exposure to light.

H. W.

**Mononitro- and Dinitro-pyrene and Amidopyrene.** By G. GOLDSCHMIEDT (*Monatsh. Chem.*, **2**, 580—586).—The two nitro-derivatives were obtained by adding very dilute sulphuric acid in a slow stream to an ethereal solution of pyrene floating on a concentrated aqueous solution of potassium nitrite, leaving the dark red liquid in a corked flask over night, then distilling off the ether, and treating the dark yellow residue with a warm mixture of equal parts of alcohol and chloroform, which left undissolved a small quantity of substance having a light yellow colour. This product, which dissolved with great difficulty in alcohol, and only in large quantities of ether, chloroform, or benzene, was recrystallised from the last-mentioned solvent, which, however, on cooling, deposited only a small quantity of the compound in small yellowish-green spherical masses; the remainder was precipitated by alcohol as a light yellow crystalline powder, which, after being separated by filtration and repeatedly boiled with alcohol, appeared under the microscope as a homogeneous mass of small needles.

The compound thus obtained is dinitropyrene,  $C_{16}H_8(NO_2)_2$ . When pure it begins to turn brown at about  $200^{\circ}$ , and decomposes slowly on further heating, so that, as observed by Graebe, who obtained this body by treating pyrene with nitric acid of sp. pr. 1.45 (*Annalen*, **158**, 292), its melting point cannot be exactly determined; it is, however, certainly higher than  $240^{\circ}$ .

The solution filtered from the dinitropyrene deposited a considerable quantity of small orange-yellow needles, which after eight or ten recrystallisations from a larger quantity of alcohol, acquired a pure yellow colour, melted constantly at  $148-149^{\circ}$ , and gave on analysis the composition of mononitropyrene,  $C_{16}H_8NO_2$ . The red colour of the solutions is due to a more soluble substance which remains in the last mother-liquors, and is left on evaporation as a semi-soft, greasy, non-crystalline, almost black mass, small quantities of which dissolve in aqueous sodium carbonate, and are precipitated therefrom by hydrochloric acid in red flocks.

*Amidopyrene*,  $C_{10}H_9NH_2$ , is formed as a hydrochloride when mononitropyrene is boiled with hydrochloric acid and tin, and is found in the precipitate formed on treating the product with hydrogen sulphide. On exhausting this precipitate with alcohol, an amber-yellow filtrate is obtained, exhibiting when hot and concentrated, a

faint blue fluorescence, which becomes stronger on dilution, and is exhibited with peculiar beauty by thin layers of the liquid. The alcoholic solution on cooling deposits the amidopyrene hydrochloride,  $C_{10}H_9(NH_2) \cdot HCl$ , in fine moderately large needles, having a faint yellowish colour. The alcoholic solution stains deal shavings deep red. The hydrochloride does not form a double salt with stannous chloride.

The free base, obtained by decomposing the hydrochloride with aqueous ammonia, and purified by dissolving it in alcohol and boiling the solution with animal charcoal, separates on diluting the liquid with water, mostly in highly lustrous quadratic laminae, which aggregate on the filter in metallicly shining films; sometimes also it is obtained in flat needles. It melts at  $116^\circ$ ; dissolves very easily in alcohol, benzene, ether, and chloroform: water dissolves only traces of it. It exhibits a blue fluorescence, stronger even than that of the hydrochloride, and increasing in brightness as the solutions are more dilute.

The *normal sulphate*,  $2C_{16}H_9NH_2 \cdot H_2SO_4$ , is formed on mixing an alcoholic solution of the base with dilute sulphuric acid, and separates as a glittering precipitate, which exhibits a very light pistachio-green colour when collected on a filter, and is seen under the microscope to be made up of perfectly regular square laminae. H. W.

**Behaviour of the Hydroxyquinone,  $C_{16}H_9(OH)O_2$ , on Oxidation.** By A. BREUER and K. ZINCKE (*Ber.*, **14**, 1896—1898).—From the hydrocarbon,  $C_{16}H_{12}$ , the authors have obtained the corresponding quinone,  $C_{16}H_{10}O_2$ , and hydroxyquinone,  $C_{16}H_9(OH)O_2$  (*Abstr.*, 1879, 327; 1880, 665). For the hydrocarbon, the formula  $Ph_2C_4H_2$  has been proposed, for the quinone  $Ph_2C_4O_2$ , and for the hydroxyquinone  $OH \cdot C_6H_4 \cdot Ph \cdot C_4O_2$ . In confirmation of these views, it was found that both the hydrocarbon and the quinone yielded the theoretical quantity of benzoic acid on oxidation, but that the hydroxyquinone yielded phthalic acid together with benzoic acid. It would rather be expected that either a hydroxybenzoic acid should be formed, or else that the benzene nucleus would be decomposed altogether. This formation of phthalic acid may be due to the proximity and ultimate interchange of the hydroxyl- with the carboxyl-group formed by the oxidation of the  $C_4O_2$  nucleus. The authors show that this phenomenon is not due to the oxidation of a hydroxybenzoic acid, for it was not found possible to convert any of the three hydroxybenzoic acids into a benzenedicarboxylic acid. By the oxidation of the hydroxyquinone with alkaline permanganate, the authors obtained no phthalic acid, but an acid allied to it. The *barium* salt of the new acid crystallises in six-sided tables, and on decomposing this salt with sulphuric acid the *pure acid* was obtained as an oil which solidified with considerable difficulty. The *potassium* salt forms white needles, the *copper* salt thick blue crystals, the silver salts a white flocculent precipitate. From the analyses of the salt the authors arrive at the formula  $C_6H_5O_5$  for the acid, which they consider to be constituted thus:  $C_6H_4 < \begin{smallmatrix} CO \cdot COOH \\ COOH \end{smallmatrix}$ ; but this view is put forward with some reserve. V. H. V.



**Essential Oil of Pistacia Lentiscus.** By F. A. FLÜCKIGER (*Arch. Pharm.* [3], 19, 170—171).—The author stated formerly that mastic contained but an exceedingly minute amount of essential oil. He has, however, since obtained samples yielding 2 per cent. of oil, also samples of the oil and of the resinous residue.

The author found (*Pharmacographia* [2], 167) that oil of Chio turpentine, which is obtained from a closely allied tree, is a true turpentine oil,  $C_{10}H_{16}$ . A column of a 100 mm. of the mastic oil was found by A. Meyer to have in Wild's polaristrobometer a dextrorotatory power of  $28^\circ$ . Raw Chio turpentine oil gave  $12.1^\circ$ ; after rectification over sodium,  $11.5^\circ$ . Jungelaussen found that mastic oil began to boil at  $155^\circ$  and distilled at  $160^\circ$ . 5 grams of it yielded 0.25 gram of terpin in well-formed crystals. Groth found these crystals to be crystallographically identical with those obtained from ordinary turpentine oil. Finally, 10 grams of the mastic oil were diluted with an equal bulk of carbon bisulphide, and saturated with dry hydrochloric acid, no solid compound was obtained however as in the case of Chio turpentine oil; but on cautiously acting with nitric acid on the dark violet tarry product in the retort, the chlorhydrate sublimed in small crystals. The essential oil of *Pistacia Lentiscus* is thus a terpene,  $C_{10}H_{16}$ ; it has a strong but agreeable odour. F. L. T.

**New Hydrocarbon from Sequoia Gigantea.** By G. LUNGE and T. STEINKAULER (*Ber.*, 14, 2202—2206).—The authors have further examined the hydrocarbon *sequoiene* obtained from the leaves of the *Sequoia gigantea* (Abstr., 1881, 98); but owing to the difficulty experienced in obtaining a sufficiently large quantity in the pure state, they have not been able to investigate thoroughly its products of decomposition. Sequoiene is insoluble in alcohol and cold concentrated sulphuric acid; with picric acid it forms red crystalline needles, with nitric acid a gold-coloured compound. On oxidation with chromic mixture, a golden flocculent substance was formed, soluble in alcohol and ether, and crystallising out from benzene in delicate, silky prisms. The results of the analysis agree best with the empirical formula,  $C_{13}H_{10}O_2$ . On examining the oils obtained from the leaves of the *sequoia*, it was found that the one of lowest boiling point (b. p.  $155^\circ$ , sp. gr. .8522) was a terpene,  $C_{10}H_{16}$ , but differed in its specific rotatory power  $[\alpha]_D = +23.8$  from other known terpenes; in chemical properties, however, it resembles the members of that class in forming a hydrochloride crystallising in white camphor-like needles. The oil of next boiling point (b. p.  $227$ — $230^\circ$ ; sp. gr. = 1.045) has the empirical formula  $C_{18}H_{26}O_3$ ; it is insoluble in water, soluble in alcohol, ether, and chloroform, insoluble in soda. The oil boiling at  $280$ — $290^\circ$  was only obtained in small quantities, and was not thoroughly examined. V. H. V.

**Campheride.** By E. JAHNS (*Ber.*, 14, 2385—2390).—The substance which Brandes (*Arch. Pharm.* [2], 19, 95) obtained from *galanga root*, and to which the name campheride was given, is a mixture of at least three different compounds. In order to prepare these bodies, *galanga root* is exhausted with alcohol (90 per cent.). The

residue which remains on evaporating the alcoholic solution is dissolved in ether, the ether is allowed to evaporate, and the viscous residue is mixed with a few drops of water and left to crystallise. The crystalline mass is washed with chloroform, and afterwards with alcohol, to remove resinous matter, and is finally recrystallised from 90 per cent. alcohol. To separate campheride from the two substances, *galangin* and *alpinin*, with which it is mixed, the crude product is dissolved in 30 parts of hot alcohol (75 per cent.): campheride is deposited from the cold solution in yellow needles. The mother-liquor is then heated and mixed with one-fifth its weight of hot water, when alpanine and galangine are deposited; on evaporating the filtrate a further crop of galangine is obtained.

*Alpanin* has not yet been obtained in a state of purity; it melts between  $180^{\circ}$  and  $190^{\circ}$ .

*Galangin* is deposited from a solution in absolute alcohol in six-sided plates (m. p.  $215^{\circ}$ ).

*Campheride*,  $C_{16}H_{12}O_6 + H_2O$ , crystallises in flat needles of a pale yellow colour, which dissolve freely in warm alcohol, ether, and glacial acetic acid. They require 400 parts of water at the ordinary temperature for solution. The crystals melt at  $221^{\circ}$ , and sublime at a higher temperature with partial decomposition. Alkalis and strong sulphuric acid dissolve campheride, forming a yellow solution. An alcoholic solution of campheride throws down orange precipitates,  $C_{16}H_{15}O_6Pb$  and  $C_{16}H_{10}O_6Ba(OH)_2$ , with lead and barium salts. *Diacetocampheride*,  $C_{16}H_{10}O_6Ac_2$ , forms colourless needles (m. p.  $188^{\circ}$ ) insoluble in water and sparingly soluble in alcohol. *Dibenzocampheride* (m. p.  $185^{\circ}$ ) resembles the preceding compound. On the addition of bromine (1 part) to a solution of campheride (2 parts) in glacial acetic acid, the dibromo-derivative,  $C_{16}H_{10}Br_2O_6$ , is deposited in yellow needles (m. p.  $224^{\circ}$ ), sparingly soluble in alcohol. Anisic and oxalic acids are formed by the action of nitric acid (sp. gr. 1.18) on campheride.

W. C. W.

**Decomposition of certain Resins by Distillation over Zinc-dust.** By K. BÖTSCH (*Monatsh. Chem.*, **1**, 609—620).—1. *Dragon's Blood*.—The crude distillate obtained by distilling this resin over zinc-dust was purified by distillation with high-pressure steam, whereupon a certain quantity of undecomposed resin remained behind; but on redistilling this residue with zinc-dust, and repeating this operation on the substance then remaining, a distillate was obtained which left no further residue on distillation with steam. The oil, which by these operations had been rendered much lighter in colour, was separated by fractionation into two portions; A boiling at  $100$ — $150^{\circ}$ , and B at  $200$ — $300^{\circ}$ .

The fraction A, freed from a small quantity of oxygenated compounds by prolonged boiling with metallic sodium in a reflux apparatus, and subsequently distilled, yields a residue consisting of a thick heavy oil, which has an aromatic odour and solidifies on cooling to a transparent vitreous mass, insoluble in alcohol, ether, &c., even after prolonged boiling, liquefying in a retort at  $300^{\circ}$ , and distilling at a very high temperature; the vapours thereby given off condense to a

colourless strong-smelling liquid, which no longer solidifies, boils at  $146^{\circ}$ , and gives by analysis the composition of styrolene or cinnamene,  $C_8H_8$ , a result which is further confirmed by its oxidation, whereby it is converted into benzoic acid. Consequently the solid residue left in the retort must consist of metastyrolene.

The compounds distilled off in the first instance from the metastyrolene were separated by systematic fractionation into toluene,  $C_7H_8$ , boiling at  $111-112^{\circ}$ ; ethyl benzene,  $C_9H_{10}$ , boiling at  $134-140^{\circ}$ , and yielding by oxidation nothing but benzoic acid; and styrolene, boiling at  $145-146^{\circ}$ .

The portion B is a dark yellow empyreumatic oil, which acts very strongly upon sodium, becoming resinised at the same time. It does not contain any compounds which crystallise out on reduction of temperature. By agitation with potash-ley, it may be separated into a phenolic compound which dissolves, and an oily liquid which may be separated from the alkaline ley by distillation with steam. By treating the residue with dilute sulphuric acid, a compound D was obtained, which when purified by repeated distillation from water, and subsequent fractionation, yielded a small quantity of a colourless oil boiling at  $236-240^{\circ}$ , and having the composition  $C_{16}H_{20}O_4$ . The portion C was also separated by repeated fractionation into two parts, one of which is a colourless very fragrant mobile oil boiling at  $214-215^{\circ}$ , and having the composition  $C_{11}H_{16}O$ ; the other an oil boiling at  $256-260^{\circ}$ , having a slight yellowish colour and a less agreeable odour than the preceding, and represented by the formula  $C_{13}H_{20}O$ . When fused with potash, it yields phthalic acid. These two bodies are perhaps homologous with the compound  $C_9H_{12}O$ , obtained by Ciamician (this Journal, 1880, Abstr., 39) on distilling gum ammoniacum over zinc-dust, and regarded by him as orthoethylphenylmethyl ether,  $C_6H_4Et.OMe$ .

The most abundant of all the volatile products obtained by distilling dragon's blood over zinc-dust is styrolene, which amounts to about 66 per cent. of the whole: next comes ethylbenzene, while the rest occur only in subordinate quantity.

Kovalevsky, who likewise obtained styrolene from dragon's blood (*Annalen*, **120**, 66), supposes that this compound occurs in the resin in the form of metastyrolene. Bötsch, however, purified his resin by solution in alcohol, in which metastyrolene is insoluble: consequently the metastyrolene which he obtained could not have pre-existed in the resin which was subjected to distillation with zinc-dust, but must be regarded as a product of decomposition, a view corroborated by the results which Hofmann and Blyth obtained (*Annalen*, **53**, 311) by the dry distillation of dragon's blood.

2. *Guaiacum*.—This resin distilled over zinc-dust yields, as chief product, creosol,  $C_8H_{10}O_2 = C_6H_3Me(OH).OMe$  (about 50 per cent.), together with toluene, metaxylene, and paraxylene (about 30 per cent.), and small quantities of pseudocumene and a solid hydrocarbon having the composition  $C_{12}H_{12}$ .

1200 grams of the purified resin yield about 350 c.c. of a dark-brown mobile oily distillate, having a strong phenolic odour, and con-

sisting for the most part of compounds heavier than water. On redistilling the crude product with steam, only the lighter compounds ( $\alpha$ ) pass over at first; and if the receiver be changed as soon as oil-drops pass over which sink in water, the specifically heavier compounds ( $\beta$ ) may easily be separated. Lastly, the condensation-water contains in solution a considerable quantity of creosol, which may be easily extracted by ether and obtained in the form of an oil boiling at  $214-216^\circ$ , and in alcoholic solution giving the characteristic green iron reaction.

The portion  $\alpha$  likewise consists for the most part of creosol, which may be removed by agitation with strong soda-ley, whereupon a crystalline mass separates, with slight rise of temperature; and on separating the undissolved oil by means of ether and evaporating off the ether, there remains a slightly brown very mobile oily liquid, separable by repeated fractionation into toluene (b. p.  $111-112^\circ$ ); meta- and para-xylene (b. p.  $136-141$ ) yielding by oxidation with chromic acid, a mixture of meta- and para-phthalic acid, and pseudocumene boiling at  $166^\circ$ .

The portion  $\beta$  likewise consists mainly of creosol, but contains also a solid hydrocarbon, which may be separated by agitating the entire liquid which has passed over at  $220-290^\circ$  with dilute soda-ley, and leaving it at rest for about 48 hours. The surface of the liquid then becomes covered with a network of crystals, which may be purified by filtration, washing, pressure between filter-paper, and repeated sublimation.

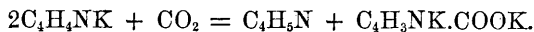
The compound thus obtained has the composition  $C_nH_n$ , and its vapour-density (determined by V. Meyer's method) shows that its molecular formula is  $C_{12}H_{12}$  (V. D. by experiment 5.35, by calculation 5.4). It crystallises in rather large, nacreous, well-defined, thin, apparently rhombic laminæ, which when recently sublimed exhibit a bluish fluorescence. It dissolves in alcohol and ether, and separates from the latter in compact strongly refracting crystals. It volatilises easily with vapour of water, melts at  $97-98^\circ$ , and sublimes at a few degrees higher; dissolves with green colour in strong sulphuric acid, and is not precipitated therefrom by water. It unites with *picric acid*, forming a compound which is sparingly soluble in alcohol, and crystallises in slender needles melting at  $123^\circ$ . These properties, together with the composition of the compound, demonstrate its identity with guaïene, the hydrocarbon which Wieser obtained by the reducing action of zinc-dust on pyroguaiacol (Abstr., 1881, 813).

The results of the preceding investigation agree to a certain extent with those which Unverdorben, Sobrero, Hlasiwetz and v. Gilm obtained by the dry distillation of guaïacum, as will be seen from the following comparison :—

Products of dry distillation.	Products of distillation over zinc-dust.
Guaiol.	Toluene. Meta- and para-xylene. Pseudocumene.
Guaiacol. Cresol. Pyroguaiacol.	Cresol. Guaiene.

H. W.

**Some Compounds of the Pyrroline Series.** By G. L. CIAMICIAN (*Monatsh. Chem.*, 1, 624—629).—When potassium-pyrroline is heated a stream of carbon dioxide, half of the pyrroline distils over, and the residue is converted into the dipotassic salt of pyrroline-carboxylic or carbopyrrolic acid; thus—



The reaction begins at 180°, but goes on best between 200° and 220°, and, with 20 grams potassium-pyrroline, is completed in three or four hours. As soon as pyrroline vapours cease to pass over, the product is left to cool in a stream of carbon dioxide, the contents of the retort are dissolved in water, and the solution, after filtration from small quantities of pyrroline, is neutralised with dilute sulphuric acid and shaken up with ether. The acid thus obtained has a brown-red colour, and still smells of pyrroline. It is best purified by dissolving it in water, decolorising with animal charcoal, precipitating with lead acetate, decomposing the precipitate with hydrogen sulphide, and agitating the filtrate with ether, whereby a less highly coloured product is obtained, which may be further purified by redissolving it in water, again decolorising with animal charcoal, and dissolving out the acid from the aqueous solution with ether.

The acid thus obtained has the composition of pyrroline-carboxylic acid,  $\text{C}_5\text{H}_5\text{NO}_2 = \text{C}_4\text{H}_4\text{N.COOH}$ . It is, however, not identical with the acid obtained by Schwanert from ammonium pyromucate (*Annalen*, 116, 274), and by Weidel and Ciamician from pyrocoll (this Journal, 1881, Abstr., 295), being distinguished therefrom by its greater instability, decomposing with red coloration and separation of carbon dioxide, when exposed to the air, when its aqueous solution is boiled, and when its ethereal solution is left to evaporate. Even in a stream of hydrogen or carbon dioxide it cannot be sublimed without considerable decomposition, whereas Schwanert's acid sublimes very readily without decomposition. When an attempt is made to sublime it by heating in a vacuum, it is completely resolved, without sensible coloration, into carbon dioxide and pyrroline. It crystallises in slender needles, and when heated in a small sealed tube, melts, with partial decomposition, at 161—162°; whereas ordinary carbo-pyrrolic acid crystallises in laminæ, and melts, with decomposition, at 191.5°. The author distinguishes the ordinary acid as  $\alpha$ -, and the acid obtained as above by heating potassium-pyrroline in carbon dioxide, as

*β-pyrroline-carboxylic* or *-carbopyrrolic acid*. The barium salt of the *β*-acid,  $(C_4H_4N.COO)_2Ba$ , crystallises in thick shining needles, whereas that of the *α*-acid forms small shining laminae.

*Potassium-homopyrroline* reacts with carbon dioxide in the same manner as potassium-pyrroline, yielding homopyrroline-carboxylic acid, the barium salt of which has the composition  $[C_4H_3(CH_3)N.COO]_2Ba$ .

The direct introduction of carbon dioxide into the potassium salts of pyrroline and homopyrroline suggests the idea that the potassium derivatives of other imides may react in like manner; and an experiment tried with this view on the potassium derivatives of carbazol or

diphenylimide,  $\begin{array}{c} C_6H_4 \\ | \\ C_6H_4 \end{array} \rangle NH$ , led, in fact, to the expected result, respecting which the author promises a further communication.

The analogy between the reaction of pyrroline and its homologues with potassium and carbon dioxide, and that of the phenols with the same bodies, induced the author to attempt the conversion of the homologues of pyrroline into the corresponding carboxylic acids by the action of melting potash.

When potassium-homopyrroline is added to melting potash, it floats at first on the liquid alkali, but, after a short time, an evolution of hydrogen is set up and continues till the oily layer has completely disappeared: on neutralising the aqueous solution of the melt with dilute sulphuric acid, and agitating with ether, a crystalline body is obtained exhibiting the properties of the pyrroline-carboxylic acids. The substance thus obtained does not, however, appear to be a single compound, but a mixture of two isomeric acids, for it melts at  $175-180^\circ$ , and appears, under the microscope, as a mixture of needles and laminae. The homopyrroline occurring in animal oil is, therefore, probably a mixture of two isomeric bodies; but further investigation is required for the satisfactory elucidation of the matter.

*Reaction of Potassium-pyrroline with Chlorinated Compounds.*—When this compound is introduced into chloroform diluted with 100 times its volume of absolute ether, the liquid becomes heated to boiling, and potassium chloride is formed, together with a body having a strong alkaline reaction; and, on agitating the filtered liquid with dilute hydrochloric acid, and distilling the acidulated solution with potash-ley, a colourless oil is obtained, smelling like pyridine and quinoline, soluble in water, boiling at about  $85^\circ$ . It contains chlorine, forms with mercuric chloride a white precipitate soluble in hydrochloric acid, and unites with that acid, forming a salt which crystallises in radiate groups of long needles, and reduces platinic chloride.

Potassium-pyrroline reacts in a similar manner with *chlor-* and *brom-acetic acid*. By its action on ethylic monobromacetate dissolved in ether, there is produced, together with potassium bromide, a viscid acid liquid, which forms a deliquescent sodium salt and a sparingly soluble silver salt, and unites with mercuric chloride, forming a compound insoluble in water, but soluble in hydrochloric acid.

*Bromine* dissolved in ether likewise acts with great violence on

potassium-pyrroline, without, however, converting it into pyrroline-red, and forms, together with potassium bromide, a brominated body soluble in ether and crystallising in needles. H. W.

### Physiological Effects and Chemical Reactions of Quinoline.

By J. DONATH (*Ber.*, **14**, 1769—1774).—The author gives an account of further experiments, the results of which confirm his former conclusions regarding the effect of quinoline on vinous fermentation and on bacteria, viz., that it is without influence on the former, but destroys the latter (*Abstr.*, 1881, 298). Quinoline may be taken internally in doses of from 1—2 grams daily, without affecting the nervous system or the mucous membrane. It also appears that quinoline, in such cases, is not found in the urine as such, but probably finds its way into the urine as pyridinecarboxylic acid.

*Chemical Reactions of Quinoline.*—Quinoline salts give with potash a white precipitate, slightly soluble in excess, but easily soluble in ether, benzene, alcohol, and less soluble in carbon bisulphide, chloroform, and amyl alcohol. Sodium carbonate gives a precipitate insoluble in excess; carbonic anhydride is liberated. Ammonia and ammonium carbonate produce precipitates soluble in excess of the reagents.

Solution of iodine in potassium iodide (7 parts of potassium iodide, 5 of iodine, and 100 of water) gives a reddish-brown precipitate, insoluble in hydrochloric acid. Limit of reaction, 1 : 25,000.

Phosphomolybdic acid (10 parts of sodium phosphomolybdate in 100 of water, acidified by nitric acid) gives a yellowish-white precipitate insoluble in ammonia. Limit, 1 : 25,000.

Picric acid (1 in 100 of water) gives a yellow amorphous precipitate, soluble in alcohol, sparingly soluble in hydrochloric acid, but soluble in potash, forming a reddish-yellow solution. Limit, 1 in 17,000.

Mercuric chloride (5 parts in 100 of water), a white flocculent precipitate, easily soluble in hydrochloric acid, slightly soluble in acetic acid. From dilute solutions it separates in needle-shaped crystals. Limit, 1 in 5,000.

Potassiomericuric iodide (5 parts of potassium iodide, 1.4 of mercuric chloride, and 100 of water) gives a yellow-white amorphous precipitate which, on addition of hydrochloric acid, is converted into amber-yellow needle-shaped crystals. Limit, 1 in 3,500.

Potassium ferrocyanide gives a reddish coloration, and on addition of a mineral acid a reddish-yellow amorphous precipitate is formed.

Potassium dichromate produces beautiful crystals, soluble in excess.

Neither tannic acid nor ferric chloride precipitates quinoline salts; neither does nitric or sulphuric acid give any coloration with these salts. P. P. B.

**Diquinoline.** By A. CLAUS (*Ber.*, **14**, 1939—1942).—In a former communication (*Ber.*, **14**, 82) the author noted that a new base, identical with the diquinoline of Williams (*Abstr.*, 1881, 613), was formed by heating quinoline hydrochloride with aniline. It has since been found that the aniline plays no essential part in the reaction: for quinoline hydrochloride, heated either by itself or with quinoline, yields the same product, although the addition of aniline is found advantageous

in liberating the base from its salts. After suitable purification, diquinoline,  $C_{18}H_{14}N_2$ , is obtained in pale golden-yellow needles (m. p.  $114^\circ$ ), insoluble in water, soluble in alcohol and ether. It dissolves in acids, forming a deep coloration which, however, does not yield salts of the base on evaporation. The platinochloride forms a golden precipitate of composition  $(C_{18}H_{14}N_2, HCl)_2, PtCl_4$ . The author considers that the platinochlorides obtained by Williams were probably due to the presence of some impurity in the base. By the oxidation of diquinoline, a crystalline acid (m. p.  $96^\circ$ ) is obtained which, although possessing the same composition as pyridinedicarboxylic acid, is not identical, but probably polymeric, with it. Further observations on this point are promised.

V. H. V.

**Conine and its Compounds.** By J. SCHORM (*Ber.*, **14**, 1765—1769).—The author describes two methods for extracting conine from hemlock-seeds. The first of these consists in mixing 100 kilos. of the seeds with 4 kilos. of sodium carbonate dissolved in water; a current of steam (3 atmos. pressure) is then passed through the mixture as long as the distillate has an alkaline reaction; the greater portion of the conine separates as an oil from the distillate. The distillate is then acidified with hydrochloric acid and evaporated to a syrupy consistency. When cold this is treated with 2 vols. of strong alcohol, and filtered from the ammonium chloride. The conine is liberated by means of soda from the residue obtained by evaporating the alcoholic solution, and then dissolved out by ether. Conhydrine often separates out from the ethereal solution: this, on evaporation, gives the conine which, after drying over potassium carbonate, is fractionally distilled, 60 per cent. passing over between  $168$ — $169^\circ$ .

The second method consists in extracting the seeds with dilute acetic acid; the solution is evaporated in a vacuum to a syrup, and the base liberated from this by magnesia, the free conine being extracted by ether as before.

Conine is a colourless oily liquid, volatile at the ordinary temperature; it combines with 25 per cent. of its weight of water, which is expelled by heat. It is soluble in 90 parts of water, and is unaltered by light. Its sp. gr. is 0.886.

The following salts have been prepared and analysed, and, in several cases, their crystalline form determined: bromide,  $C_8H_{13}N.HBr$ ; iodide,  $C_8H_{13}N.HI$ ; acid tartrate,  $C_8H_{13}N, C_4H_6O_6 + 2H_2O$ : the neutral oxalate,  $(C_8H_{13}N)_2H_2C_2O_4$ .

P. P. B.

**Paraconine.** By A. MICHAEL (*Ber.*, **14**, 2105—2110).—By heating a mixture of butylidene bromide (made by the action of phosphorus chlorobromide on butaldehyde) with strong alcoholic ammonia at  $200^\circ$ , paraconine is produced; the author has already prepared this substance in the same way from butylidene chloride.

By reducing paraconine with tin and hydrochloric acid, a base is obtained which forms a crystalline methiodide, and is regarded by the author as perhaps identical with conine; by careful oxidation of paraconine, butyric acid was obtained, and also a small quantity of an acid which evolved a pyridine odour when distilled over lime.



Isoamylidene bromide and chloride when heated with ammonia also yield high-boiling bases. D. A. L.

**The Specific Gravity of Nicotine and of its Aqueous Solutions.** By J. SKALWEIT (*Ber.*, **14**, 1809—1810).—The sp. gr. of nicotine is found to be 1.0111 at 15°, a number differing considerably from that given by other investigators. Moreover, the author has observed that when water is added to nicotine, heat is produced and a diminution in volume takes place. A mixture of 100 grams of nicotine with 5 grams of water has a sp. gr. of 1.107, the sp. gr. increasing with each addition of water; a mixture containing 100 of nicotine and 70 of water, has a sp. gr. 1.033. Conine, on the other hand, appears to suffer a diminution in sp. gr. when mixed with water.

P. P. B.

**Tropine.** By A. LADENBURG (*Compt. rend.*, **93**, 517—520).—When tropine is heated with methyl iodide it yields an additive product which separates from alcohol in large cubic crystals. When heated with silver oxide, it gives methyltropineammonium, and the solution if distilled yields a methyltropine,  $C_8H_{17}NO$ , as a basic oil. The aurochloride is precipitated from a hydrochloric acid solution in the form of an oil, which, after a time solidifies and forms fine crystals. Methyltropine combines with methyl iodide, and the additive product so obtained, on treatment with an aqueous solution of silver oxide, yields silver iodide and a product which decomposes on distillation into trimethylamine, a hydrocarbon, and an oxygenated compound. The first is formed in considerable quantity. The hydrocarbon is found in traces only, and has not been obtained pure. The oxygen compound,  $C_7H_{10}O$ , is an oil (b. p. 180°) having the odour of acetone. The author is endeavouring to prepare methyltropine synthetically. He has already combined  $C_7H_{10}O$  with dimethylamine by heating at 80°, and has obtained a base boiling below 200°, and giving an aurochloride resembling that of methyltropine. He also attempted to obtain the corresponding compound with trimethylamine, but only traces of a base were found.

J. I. W.

**Decomposition of Tropine.** By A. LADENBURG (*Ber.*, **14**, 2403—2406).—Tropilene,  $C_7H_{10}O$ , and tropilidene,  $C_7H_8$ , formed by the decomposition of tropine, can be obtained in larger quantities from monomethyltropidine iodide and dimethyltropine iodide.

Tropilene is slowly dissolved by an aqueous solution of dimethylamine, with the formation of  $\beta$ -methyltropine,  $NMe_2.C_7H_{10}OH$ . This base is an oily liquid (b. p. 198—205°) which is distinguished from  $\alpha$ -methyltropine (b. p. 243°) by the ready solubility of the latter in water. Hydrochloric acid decomposes  $\beta$ -methyltropine, forming tropilene and dimethylamine. Under similar conditions  $\alpha$ -methyltropine splits up into methyl-chloride and tropidine.

W. C. W.

**Tropine.** By G. MERLING (*Ber.*, **14**, 1829—1833).—*Methyltropine iodide*,  $C_8H_{15}NOMeI$ , is obtained by the action of methyl iodide on tropine, it crystallises from dilute alcohol in small shining cubes. It does not combine with more methyl iodide, showing tropine to be a

tertiary base. The *platinochloride*,  $(C_8H_{15}NOMeCl)_2PtCl_4$ , crystallises from hot aqueous solutions in orange-yellow prisms.

*Methyltropine* is obtained by distilling the methyltropine hydrate prepared from the above-mentioned iodide; it has been obtained in the form of an oily liquid boiling at  $240-245^\circ$ . Trimethylamine is also found amongst the products of distillation.

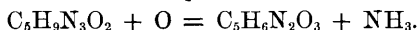
*Dimethyltropine iodide*,  $C_8H_{14}Me_2NOI$ , is obtained by the action of methyl iodide on methyltropine; it forms colourless, deliquescent needles, sparingly soluble in cold alcohol and insoluble in ether. Its *platinochloride*,  $(C_8H_{14}Me_2NOCl)_2PtCl_4$ , crystallises from dilute alcohol in orange-yellow crystals. Dimethyltropine hydroxide has been prepared, and submitted to distillation; amongst the products of distillation were found trimethylamine, and an oily liquid insoluble in acids and having an odour resembling that of peppermint; it unites directly with bromine.

The author concludes that the constitutional formula of tropine is probably  $C_8H_9ONMe_2$ , and that of methyltropine  $C_8H_8MeONMe_2$ .

P. P. B.

**Caffeine.** By E. FISCHER (*Ber.*, **14**, 1905—1915).—A continuation of the author's researches (*Abstr.*, 1881, 614) on the derivatives of caffeine. He incidentally recommends that in the preparation of hypocaffeine, diethoxyhydroxycaffeine should be directly obtained by the action of bromine on hydroxycaffeine in alcoholic solution, without the isolation of the intermediate bromo-derivative.

Hypocaffeine has acid properties; its barium salt is soluble in water, sparingly soluble in alcohol; its silver salt, crystallising in white tables, is sparingly soluble in cold water. Hypocaffeine is not attacked by the strongest oxidising or reducing agents. By heating hypocaffeine with baryta-water, or better with basic acetate of lead, *caffoline* is obtained among other products. This substance crystallises in long white prisms (m. p.  $194-196^\circ$ ) of composition  $C_8H_9N_3O_2$ , soluble in water, sparingly soluble in alcohol; it differs from hypocaffeine in its instability in the presence of acids. By heating with baryta-water, it is slowly decomposed into ammonia, methylamine, carbonic and oxalic acids; by warming with hydriodic acid it is converted into monomethylcarbamide. On oxidising caffoline with chromic acid mixture, chlorestrophan is formed, thus:



From these various reactions it appears to the author that caffoline

contains the grouping

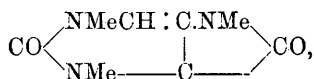
$$\begin{array}{c} C-NMe \\ | \\ N-C-NMe \end{array}.$$

*Caffuric acid*,  $C_8H_9N_3O_4$ , is obtained as a subsidiary product from the mother-liquors in the preparation of hypocaffeine, it forming splendid glistening tables which immediately deliquesce and lose their transparency; it melts between  $210-220^\circ$  with decomposition; it has feeble acid properties, the barium salt being easily decomposed by carbonic acid; its silver salt,  $C_8H_9N_3O_4Ag$ , crystallises in colourless transparent tables. By hydriodic acid, caffuric acid is reduced to *hydrocaffuric acid*,  $C_8H_9N_3O_3$ , which forms colourless needles (m. p.

245°). Caffuric acid is easily decomposed by basic lead acetate into mesoxalic acid, methylamine, and monomethylcarbamide, thus:  $C_6H_4N_3O_4 + 3H_2O = C_3H_4O_6 + NH_2Me + C_2H_5N_2O$ .

The formation of methylurea from caffeine, as well as from caffuric acid by relatively simple reactions, leads to the supposition that the former contains, besides a dimethylalloxan group, a methylcarbamide residue. Rochleder (*Annalen*, **71**, 9) has observed that caffeine is decomposed by chlorine-water into tetramethylalloxantin, cyanogen chloride, and methylamine; but these, the author finds, are products of a secondary reaction; for by the action of hydrochloric acid and potassium chlorate on caffeine, there are formed dimethylalloxan and monomethylcarbamide.

As this reaction is precisely analogous to the decomposition of uric acid into alloxan and carbamide, there can be no doubt that the arrangement of atoms in uric acid and caffeine is similar, and that the latter is the diureide of mesoxalic acid. From this result, together with others obtained in the study of caffeine, and detailed either in this or the former communication, the author assigns to caffeine the following constitutional formula:—



which resembles the formula proposed by Medicus (*Annalen*, **175**, 280).  
V. H. V.

**A New Series of Bases Derived from Morphine.** By E. GRIMAUZ (*Compt. rend.*, **93**, 591—593).—The author finds that when codeine methiodide is heated with silver oxide, it yields codeine methoxide,  $C_{18}H_{20}NO_2(OMe)$ . The new salt crystallises in brilliant needles (m. p. 118·5°). The base is precipitated from solutions of its salts by ammonia, thus differing from codeine and codethylene. The methyl base can also be prepared by the action of potash on codeine methiodide; but the yield is not so good as when silver oxide is employed.

The author has also prepared codethylene methiodide. It resembles codeine methiodide. When heated with silver oxide or potash, it is converted into a crystalline tertiary base (m. p. 132°) resembling codeine methoxide, but more soluble in ether. It gives a violet coloration with sulphuric acid. It is probably methylcodethylene.

The method of preparation affords a general reaction by which the homologues of codeine containing new alcohol groups in the morphine nucleus can be obtained.  
J. I. W.

**Some Compounds of Quinine.** By Z. H. SKRAUP (*Monatsh. Chem.*, **2**, 610—614).—*Quinine diethiodide*,  $C_{20}H_{24}N_2O_2(Et)_2 + 3H_2O$ , is formed, with separation of potassium iodide, when an alcoholic solution of quinine is heated for eight hours with potash and excess of ethyl iodide. The brown solution decanted and evaporated over sulphuric acid leaves brownish crystals, which may be freed

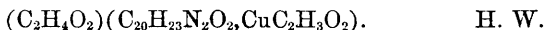
from a trace of resinous impurity by solution in hot water, and by repeated crystallisation from dilute alcohol. The product may be ultimately obtained in pure yellow crystals, mostly having a tabular development. Heated under water, they melt to a yellowish-brown oil, which on agitation easily mixes with the supernatant liquid, the colour then disappearing completely; they also dissolve readily in alcohol whether anhydrous or hydrated, but are insoluble in ether. They give off their water at  $100^{\circ}$ , become reddish at the edges even below that temperature, and fuse at  $115^{\circ}$  to a reddish-yellow mass, which, when drenched with water, gradually becomes pure yellow and crystalline, and subsequently dissolves, the solution when left to evaporate again depositing the above-described yellow crystals.

These crystals are monoclinic, having the axial ratio  $a : b : c = 1.7291 : 1 : 1.2135$ , and this may be  $ac = 107.6$ . Observed faces 100, 001, 110, 111, or  $\infty P\infty$ ,  $0P$ ,  $\infty P$ ,  $P$ , the basal face predominating.

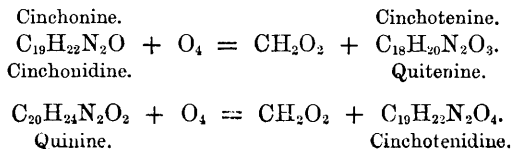
*Quinine with Cupric Acetate*,  $C_{20}H_{24}N_2O_2, Cu(\text{AcO})_2$ .—A dilute alcoholic solution of quinine mixed with cuprammonium acetate, and left to evaporate over sulphuric acid, deposits this compound after some days in small green crystals which appear to contain water, become bluish-green when left over sulphuric acid, but recover their original colour in a few seconds on exposure to the air.

*Quinine with silver nitrate*,  $C_{20}H_{24}N_2O_2, AgNO_3$ , is prepared like the copper salt, and agrees in solubility with the isomeric compound of quinidine (Hesse's conquinine) with silver nitrate prepared by Stenhouse.

A dilute alcoholic solution of quinine mixed with a little more than 1 mol. ammonia, and then with a large excess of silver nitrate, deposited a white gelatinous precipitate, which, after washing with dilute alcohol and drying, had approximately the composition of *argentoquinine*,  $C_{20}H_{23}AgN_2O_2$  (exp. 26.5 per cent. Ag; calc. 25.06). Hence it appears probable that the two salts above described may be regarded as quinine salts, in which 1 atom of hydroxylic hydrogen is replaced by an equivalent quantity of metal, viz., the silver salt as  $NO_3H, C_{20}H_{23}N_2O_2Ag$ , and the copper salt as



**Quinine and Quinidine.** By Z. H. SKRAUP (*Monatsh. Chem.*, **2**, 587—609).—The author has shown by former experiments (Abstr., 1880, 409) that the three cinchona alkaloids, quinine, cinchonine, and cinchonidine, exhibit a remarkable agreement in their behaviour with potassium permanganate, all three when subjected to limited oxidation with this reagent giving up 1 atom of carbon in the form of formic acid, and being converted, by assumption of 2 atoms of oxygen, into weak bases of phenolic character, thus:—



This resemblance extends, moreover, to quinidine (Hesse's conquinine), a base isomeric with quinine, inasmuch as Pawlowsky has obtained from this base, together with formic acid, a base analogous in composition to quitenine, and in all probability isomeric therewith. Hence it appears that all these four alkaloids have one of their carbon-atoms in peculiar and similar situations, but the experiments hitherto made do not give any further information as to their chief isomeric relations. To throw further light on this question, quinine and quinidine were subjected to oxidation with chromic acid in the same way as cinchonine and cinchonidine were formerly treated.

*Oxidation of Quinine.*—10 parts quinine sulphate,  $C_{20}H_{24}N_2O_2 \cdot H_2SO_4 + 2Aq$ , are dissolved in a mixture of about 30 parts strong sulphuric acid and 200—250 parts water; the liquid is heated to boiling, and an aqueous solution of 20 parts chromic acid is added in a slow stream, or by successive small portions. After 2 or  $2\frac{1}{2}$  hours' boiling the undecomposed chromic acid is reduced by addition of a little alcohol, the green liquid is immediately stirred into a cold solution of 80—90 grams potash in half a litre of water, and the clear green alkaline solution is heated to boiling, best in a copper vessel, till the precipitation of ebromic oxide is complete. The yellow liquid may then be separated from the precipitate by syphoning, washing by decantation, and finally on a strainer with gradual pressure, and after complete neutralisation, left to evaporate over sulphuric acid, its reaction being tested from time to time, and kept slightly alkaline rather than acid. The concentration having been continued till two or three crops of potassium sulphate have separated out, the last mother-liquor is mixed with an equal volume of alcohol; the dark-brown solution, after standing for several hours, is separated from the precipitated potassium sulphate; the alcohol is driven off by distillation and evaporation over the water-bath, and the acid resulting from the oxidation of the quinine is set free by addition of hydrochloric or sulphuric acid. The chief product of the reaction is then soon precipitated in brownish granules, which attach themselves chiefly to those parts of the vessel which have been scratched by the glass rod, and the precipitation is completed in six or eight hours. The product amounts to 50 to 55 per cent. of the calculated quantity. The dark-brown mother-liquor contains a second body of acid nature; but, as in the case of cinchonine and cinchonidine, all attempts to separate this second product of oxidation in definite form proved fruitless; it appears, however, to be very similar to the amorphous body obtained in the oxidation of cinchonine and cinchonidine. The only other products of the oxidation were carbonic and formic acids.

*Oxidation of Cinchonidine.*—This base treated as above yielded the same crystallised acid, together with amorphous products, which could not be separated in definite form.

**QUININIC ACID,  $C_{11}H_9NO_3$ .**—This acid, homologous with cinchoninic acid, is the crystallised oxidation-product above mentioned. It is best purified by recrystallisation from hot dilute hydrochloric acid, finally with addition of animal charcoal; the purification may, how-

ever, also be effected by combining the quinic acid with hydrochloric acid, and decomposing the resulting compound with water.

Pure quinic acid crystallises in long thin faintly yellowish prisms, which dissolve very sparingly in cold, and but little more readily in hot water; abundantly and with yellowish colour in dilute hydrochloric or sulphuric acid, much less easily in acetic acid; readily and without colour in alkaline solvents; ether and benzene dissolve only traces of it.

Quinic acid dissolves but sparingly in alcohol, even at the boiling heat, forming a solution which exhibits a blue fluorescence exceeding that of quinine salts in beauty and sensibility. In comparatively strong solutions it is pure blue, but passes somewhat into violet on dilution, disappears on addition of  $1\frac{1}{2}$  vol. water, is regenerated by alcohol, and entirely destroyed on addition of a drop or two of sulphuric acid to the alcoholic solution. Chromic oxide is obstinately retained by quinic acid, and cannot be completely removed from it, even by repeated crystallisation from glacial acetic or dilute hydrochloric acid; conveniently, however, by repeated crystallisation of the calcium salt.

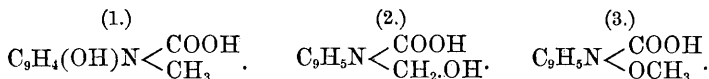
Quinic acid heated in capillary tubes melts with decomposition at  $280^{\circ}$ . When cautiously heated in a small flask, it melts to a yellowish-brown liquid, and then sublimes partially, a considerable portion being, however, decomposed and giving off a pungent vapour of disagreeable odour, which is emitted much more characteristically on heating the metallic quinates, and is undoubtedly due to quinolide,  $C_9H_9NO$ , the base which Butlerow and Wischnegradsky obtained, with separation of carbonic anhydride, by the action of alkalis on quinine (this Journal, 1879, Abstr., 988).

Quinic acid in its double character of carboxylic acid and nitrogenous base, forms two classes of salts. Those which are formed by substitution of metal for hydrogen are colourless both in the solid form and in solution, unless the metal itself imparts a peculiar colour. The compounds with acids are all yellow.

The *silver salt*,  $C_{11}H_8AgNO_3$ , is a crystalline powder not affected by light. The *calcium salt*,  $(C_{11}H_8NO_3)_2Ca + 2H_2O$ , is moderately soluble in cold, more freely in hot water, and crystallises in flat rosettes of white needles, which give off their water between  $160^{\circ}$  and  $200^{\circ}$ . On heating this salt or any other quinate, an oil distils over, having a fragrant odour somewhat like that of coumarin. The *barium salt*,  $(C_{11}H_8NO_3)_2Ba + 4H_2O$ , is very much like the calcium salt in appearance, but much more soluble even in cold water. Both these salts, like the free acids, obstinately retain chromic oxide. *Copper salt*. A solution of quinic acid in strong acetic acid mixed with cupric acetate deposits after a while needles of the free acid, and the green filtrate when left to evaporate deposits needles of a dark grass-green colour mixed with yellowish crystals. The solution of the ammonium salt yields, on addition of cupric acetate, a light-green flocculent precipitate, which on standing, and almost instantly on heating, changes to a heavy powder composed of grey-violet crystals, nearly insoluble in water, and becoming light lavender-blue when dried. Their composition is represented by the formula  $(C_{11}H_8NO_3)_2Cu + 1\frac{1}{2}H_2O$ .

*Hydrochloride of Quininic Acid*,  $C_{11}H_9NO_3.HCl$ .—This salt, formed by direct combination, separates in well-defined yellow triclinic crystals mostly of tabular habit, and containing 2 mols.  $H_2O$ . They dissolve without alteration in a small quantity of water, but on evaporating the solution, free quinic acid separates out. The *platinochloride*,  $(C_{11}H_9NO_3)_2H_2Cl_6Pt$ , is precipitated, on adding platinic chloride to a hot moderately dilute solution of the hydrochloride, in long light-yellow needles containing  $4H_2O$ , frequently, however, mixed with thick prisms of a darker colour. The anhydrous salt separates from the mother-liquor in orange-red prisms, and is also formed directly when an excess of hydrochloric acid is used in the preparation.

The intimate relations existing between quinine and quinidine on the one hand, and cinchonine and cinchonidine on the other, render it probable that a similar relation exists between the several oxidation-products, and accordingly that quinic acid has a constitution similar to that of cinchoninic acid (Abstr., 1880, 409), and may be regarded as a substituted quinoline-monocarboxylic acid. Such a compound might take either of the three following forms:—

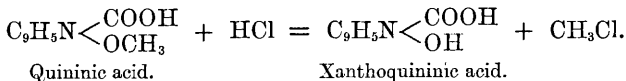


In other words quinic acid may be regarded as the monocarboxylic acid, either of a lepidine-phenol or of a quinoline-carbinol, or of the methylic ether of a hydroxyquinoline. If it be correctly represented by the first or the second of these formulæ, it should be possible to introduce an acetyl-group into the molecule by substitution of  $OAc$  for  $OH$  in the pyridine-nucleus or the benzene-nucleus of the first, or in the  $CH_2.OH$  group of the second; but all attempts to effect this substitution have proved fruitless, so that there remains only the third formula as the true representative of the constitution of quinic acid.

*Oxidation*.—Nitric acid does not act upon quinic acid even when heated, but chromic acid attacks it after boiling for a short time. The oxidation is, however, much better effected by potassium permanganate, a 3 per cent. solution of which added to a solution of quinic acid in potash, in such proportion that 3 atoms of oxygen shall come into action, converts it into pyridine-tricarboxylic acid,  $C_9H_7N(COOH)_3$ , the same product that is obtained in like manner from cinchoninic acid and from quinine, quinidine, cinchonine, and cinchonidine (Abstr., 1880, 895). In this last case there can be no doubt that the alkaloids are first converted into quinic and cinchoninic acids respectively, which are then further oxidised to pyridine-tricarboxylic acid. A second acid was also formed in the above reaction, but not in sufficient quantity for distinct characterisation.

*Action of Hydrochloric Acid*.—When quinic acid (1.5 gram) is sealed up in a tube with hydrochloric acid of ordinary strength (15 c.c.), and heated for five or six hours at  $220-230^\circ$ , methyl chloride escapes on opening the tube, and the liquid contents yield sooner or later a mass of laminar crystals, which may be freed from the liquid by

filtration and washing with strong hydrochloric acid, and purified by recrystallisation from dilute hydrochloric acid. These crystals consist of an acid which forms yellow salts, and may therefore be called *xanthoquininic acid*. It dissolves readily in alkalis and in mineral acids, and always with yellow colour; in glacial acetic acid and other organic acids, it dissolves readily when heated, likewise yielding yellow solutions. It is not fluorescent. Heated above  $300^{\circ}$ , it melts with partial decomposition, and at a higher temperature sublimes, gives off vapours smelling like creosote, and decomposes in a manner which will be presently specified. It crystallises without water of crystallisation, and gives by analysis numbers agreeing with the formula  $C_{10}H_7NO_3$ . Its formation from quininic acid is represented by the equation—



and affords further confirmation of the constitution previously assigned to quininic acid.

*Silver xanthoquininate*,  $C_{10}H_6AgNO_3 + 2H_2O$ , obtained by precipitation from an ammoniacal solution of the acid, is a white flocculent precipitate, which afterwards becomes yellowish, and gives off its water over sulphuric acid. The *copper salt*,  $(C_{10}H_6NO_3)_2Cu + H_2O$ , obtained in like manner, is yellow and flocculent at first, but on standing, or immediately when gently heated, changes to a heavy dark-green crystalline powder, nearly insoluble in water. The *calcium salt*,  $(C_{10}H_6NO_3)_2Ca + 10H_2O$ , and the *barium salt* with  $6H_2O$ , are both sparingly soluble, and are obtained by precipitation, the former as a thick pulp of straw-yellow needles, the latter in dull yellow crystalline crusts.

The *hydrochloride*,  $C_{10}H_7NO_3.HCl + 2H_2O$ , separates from dilute solutions containing but little free acid, in golden-yellow needles; from stronger and more acid solutions in darker-coloured laminæ. The crystals give off half their water over sulphuric acid in 48 hours, and in two hours when dried at  $100^{\circ}$ , the rest only after long-continued heating at  $110$ – $120^{\circ}$ , part of the hydrochloric acid being given off at the same time. The *platinochloride* forms a network of yellow-brown shining needles, having the somewhat unusual composition



The *sulphate*  $(C_{10}H_7NO_3)_2.H_2SO_4 + 3H_2O$ , obtained by treating xanthoquininic acid with sulphuric acid and alcohol, forms yellow crystals, which give off 2 mols. water at  $130^{\circ}$ , the remainder at  $190^{\circ}$ .

*Decomposition of Xanthoquininic Acid by Heat*.—When this acid is heated above  $300^{\circ}$ , it liquefies, and is decomposed, with rapid evolution of carbonic anhydride, leaving a residue consisting of a hydroxyquinoline,  $C_{10}H_7NO_3 = CO_2 + C_9H_7NO$ .

The preceding results show that quininic acid is a carboxylated and methoxylated derivative of quinoline; or less probably of a base isomeric therewith. The conversion of quininic acid into a pyridine-tricarboxylic acid identical with that which is obtained in like manner



from cinchoninic acid, points to the conclusion that quinoline, which forms part of the cinchonine-molecule, is also contained in the residue which yields quinic acid; further, that the methoxyl-group of the last-mentioned acid must be contained, not in the pyridine-ring, but in the benzene-ring of that compound. Lastly, it follows that the carboxyl-group of quinic acid is directly attached to the pyridine-residue, and in a position similar to that which is occupied by the carboxyl-group of cinchoninic acid.

H. W.

**Constitution of Cinchonine.** By W. KOENIGS (*Ber.*, **14**, 1852—1859).—At the outset, the author gives a brief historical account of the various researches which have thrown light on the constitution of the cinchona alkaloids and their derivatives. Of the constitution of cinchonine two opposed views have been held, according to one of which cinchonidine contains two quinoline residues. But as the decomposition of cinchonine into ethylpyridine, quinoline, and fatty acids is difficult to reconcile with this view, Wischnegradsky has proposed the formula  $C_9H_7MeN.CO.C_2H_4.C_6H_5EtN$ . The author, however, believes that this decomposition can be explained by the violent action of the melted alkali on a reduced quinoline residue, and that the supposition of the quinoline residues in cinchonine is not therefore untenable. In order to decide this question, he has conducted a series of reactions which, although not conclusive, yet point to the presence in cinchonine of two quinoline residues, one a tetrahydroquinoline, the other a methyltetrahydroquinoline. By the action of phosphorus pentachloride on cinchonine hydrochloride, the author has obtained a cinchonine chloride,  $C_{19}H_{21}N_2Cl$  (*Abstr.*, 1880, 675). By heating this latter compound with alcoholic potash, a new base,  $(C_{10}H_{20}N_2)$ , *cinchene*, is obtained, which crystallises in the rhombic system (m. p. 123—125°). By the action of nitric acid on cinchene at 220°, a gas burning with a green flame was obtained, probably methyl chloride. This renders it probable that there is in cinchene and cinchonine a  $CH_3$ -group attached to a nitrogen-atom. The production of formic acid by the gradual oxidation of cinchonine and quinine by permanganate lends additional support to this view (*Abstr.*, 1879, 656, 809, 948). By heating cinchene with hydrochloric acid, a golden crystalline, sparingly soluble hydrochloride of a new base, *apocinchene*,  $C_{18}H_{17}NO$ , is obtained. Apocinchene has the character of an amidophenol; it crystallises from hot alcohol, and melts at 209°. By oxidation with chromic mixture, apocinchene gives cinchonic, carbonic, and some small quantity of acetic acid. In the formation of apocinchene, the ethylpyridene residue of cinchene has probably given off its nitrogen in the form of ammonia or methylamine, a view which is in accordance with the experiments of Hoogewerff and v. Dorp on the oxidation of the cinchona alkaloids with alkaline permanganate, whereby half the nitrogen was evolved as ammonia, and half appeared in the pyridenetetracarboxylic acid (*Abstr.*, 1880, 895). It is further probable, from a consideration of Hofmann's experiments on the methylated derivatives of pyridene and conine, that cinchene and apocinchene contain, besides a quinoline nucleus, a reduced pyridene residue, which has a methyl group attached to a nitrogen-atom of a tertiary

amine. As nitrous acid has no action on cinchene, cinchonidine, and quinine, it is probable that both the nitrogen-atoms belong to a tertiary amine grouping. Apocinchene, from its analogy with amidophenol, contains a hydroxyl grouping possessing acid properties.

By fusing apocinchene with potash, a new base, *oxyapocinchene*,  $C_{18}H_{17}NO_2$ , is obtained, which can be crystallised from hot alcohol, and melts at  $267^\circ$ . Cinchonine differs from cinchene by a molecule of water, and these bases appear to bear to one another a relation similar to that existing between camphor and cymene. The author promises further researches, with a view of establishing the constitution of cinchonine and the substances derived from it, which are described in the present communication.

V. H. V.

**$\beta$ -Cinchoninesulphonic Acid and its Derivatives.** By H. WEIDEL (*Monatsh. Chem.*, 2, 565—579).—The author, in conjunction with Cobenzl (Abstr., 1881, 742),\* by heating cinchoninic acid with sulphuric anhydride, obtained a sulphonic acid designated as  *$\alpha$ -cinchoninesulphonic acid*, from which they prepared a hydroxy-acid, and therefrom a phenol of quinoline. It was found, however, that when the reaction took place at a very high temperature, other products were formed, and the author now finds that the acid formed under these circumstances is an isomeride of  *$\alpha$ -cinchoninesulphonic acid*, which he distinguishes by the prefix  $\beta$ .

$\beta$ -Cinchoninesulphonic acid is formed by the action of a mixture of oil of vitriol and phosphoric anhydride on cinchoninic acid at  $250$ — $260^\circ$ , but a much better mode of preparation is to heat the cinchoninic acid in a sealed tube at  $260$ — $270^\circ$  for eight or ten hours with oil of vitriol rich in sulphuric anhydride. The sulphonic acid thus obtained may be purified by mixing it with a small quantity of a dilute solution of basic lead acetate, freeing the filtrate from excess of lead by hydrogen sulphide, filtering again, and evaporating the clear liquid to the crystallising point. It then solidifies to a magma of yellowish-white, very brilliant wavelitic needles, which may be rendered quite colourless by recrystallisation with the aid of animal charcoal.

Pure  $\beta$ -cinchoninesulphonic acid forms a network of slender colourless needles, having the composition  $C_{10}H_6NO_2 \cdot SO_3H + 2H_2O$ , and giving off their water at  $130^\circ$ ; it is easily soluble in warm, less readily in cold water and alcohol. The dehydrated acid may be heated somewhat strongly, without decomposition, but ultimately turns brown, swells up in a peculiar manner without actually melting, and finally burns away, leaving a porous cinder. It has an intensely bitter taste, and acts strongly on litmus. Its aqueous solution is not precipitated by normal lead acetate, either at ordinary or at higher temperatures, but with basic lead acetate it gives a bulky precipitate, soluble in excess of the precipitant, and in normal lead acetate. Cupric acetate added to a boiling concentrated solution of the acid, forms a light blue crystalline precipitate, and silver nitrate a white crystalline precipitate, which is not affected by light. The chlorides of calcium and barium

\* In the abstract here referred to the sulphonic acid in question is erroneously stated to be obtained by the action of sulphuric acid on cinchonine.

do not precipitate the acid either in the free state or when neutralised with ammonia.

The conversion of the  $\alpha$ - into the  $\beta$ -acid by the action of sulphuric anhydride at high temperatures, which is analogous to that of *ortho*- into *para*-phenolsulphonic acid, is a very definite reaction, and is attended with the formation of only small quantities of humous products, and a syrupy sulphuretted acid substance.

The *acid ammonium salt* of  $\beta$ -cinchoninesulphonic acid is formed when a solution of the acid supersaturated with ammonia is left to evaporate over sulphuric acid at ordinary temperatures, and crystallises in slender white silky needles, having in the air-dried state the composition  $C_{10}H_5NO_2 \cdot SO_3NH_4 + 2H_2O$ , and giving off their crystal-water at  $100^\circ$ . The normal ammonium salt has not been obtained. The *barium salt*, obtained by saturation, crystallises in microscopic truncated prisms, which, when once separated, are nearly insoluble in water. The air-dried salt contains  $C_{10}H_5(NO_2)SO_3Ba + H_2O$ , and does not give off its water till heated to  $250^\circ$ . The *lead salt*, also prepared by neutralisation, separates on cooling from a concentrated solution, in small irregular laminae, having a splendid nacreous lustre, and, like the barium salt, dissolving with great difficulty when once separated. Air-dried, it has the composition  $C_{10}H_5(NO_2)SO_3Pb + 4H_2O$ , and gives off its water at  $150^\circ$ .

*$\beta$ -Hydroxycinchoninic acid*,  $C_{10}H_7NO_3 = C_{10}H_6NO_2 \cdot OH$ , is prepared like the corresponding  $\alpha$ -acid,\* by fusing  $\beta$ -cinchonine-sulphonic acid with an equivalent quantity of potash (10 g. sulphonic acid with 50 g. KOH) dissolved in a small quantity of water, stopping the operation as soon as all the water is evaporated and the melt begins to froth. On dissolving the product in a little water, and exactly neutralising with sulphuric acid, potassium sulphate and the hydroxy-acid are thrown down together, and the precipitation of the latter may be completed by cooling with ice. The hydroxy-acid may then be dissolved out by large quantities of boiling alcohol, and remains on evaporation in light yellow crusts, which may be purified by five or six crystallisations from boiling water. The acid is thus obtained in small yellowish-white, glittering, lozenge-shaped plates, belonging to the monoclinic system. It is nearly insoluble in cold water, and only slightly soluble in hot water and in alcohol, but dissolves with comparative facility, with the aid of heat, in glacial acetic acid, and in mineral acids. When heated, it partly sublimes, then melts with partial decomposition, and volatilises completely. Heated in sealed capillary glass tubes, it melts at a temperature above  $315^\circ$ , perhaps about  $320^\circ$ . The aqueous solution of the acid forms with silver nitrate after a few minutes, a white crystalline precipitate; with basic lead acetate a yellowish precipitate is formed, soluble in a large excess of the reagent; no precipitate with normal lead acetate, and no coloration with ferric chloride or ferrous sulphate. The air-dried acid contains 1 mol.  $H_2O$ , which is given off slowly at  $100^\circ$ , readily at  $105^\circ$ .

\* Abstr., 1881, 743. The name  *$\alpha$ -hydroxycinchonic acid* there given to the acid in question is inappropriate: for cinchonic acid is a non-azotised acid,  $C_{11}H_{11}O_9$ , and the proper designation of the acid  $C_{10}H_7NO_2$  is *cinchoninic acid*.—H. W.

$\beta$ -Hydroxycinchoninic acid unites, like the  $\alpha$ -acid, both with bases and with strong acids. The *normal barium salt*,  $C_{10}H_7BaNO_3$ , forms yellowish-white indistinctly crystalline crusts. The *hydrochloride*,  $C_{10}H_7NO_3 \cdot HCl$ , formed by dissolving the  $\beta$ -acid in hot strong hydrochloric acid, crystallises in a mass of slender faintly yellow very brilliant monoclinic needles, containing 1 mol.  $H_2O$ , which is given off on heating. It is completely decomposed by water. The *platinochloride*,  $(C_{10}H_7NO_3 \cdot HCl)_2 \cdot PtCl_4 + 2H_2O$ , forms small yellow shining plates, apparently monoclinic, which give off their crystal-water at  $105^\circ$ , and are decomposed by water.

$\beta$ -Hydroxyquinoline or  $\beta$ -quinophenol,  $C_9H_7NO \equiv C_9H_6N.OH$ , is formed like the  $\alpha$ -modification, by repeated dry distillation of  $\beta$ -hydroxycinchoninic acid, the crude product after the third distillation being purified by crystallisation from dilute alcohol. It is thus obtained in slender, colourless, apparently prismatic needles, having a silky lustre. It smells faintly like honey when cold, but emits a pungent phenolic odour when heated. It dissolves, not only in alcohol, but at the boiling heats, also in benzene and chloroform; somewhat less readily in ether. When heated, it partly sublimates before melting, in slender white feathery crystals. When quite pure, it melts at  $191$ – $192^\circ$ , but a small quantity of impurity lowers the melting point to  $176$ – $181^\circ$ . Its boiling point is above  $300^\circ$ , apparently between  $310^\circ$  and  $320^\circ$ . Its aqueous solution has a neutral reaction, and precipitates silver, copper, and lead salts; it does not give any colour-reaction with ferric chloride or ferrous sulphate.

The *hydrochloride*,  $C_9H_7NO \cdot HCl$ , crystallises in very long capillary, flexible, colourless needles, very easily soluble in water and in alcohol. The *platinochloride*,  $(C_9H_7NO \cdot HCl)_2 \cdot PtCl_4$ , forms needle-shaped crystals containing 2 mols. water, which they give off at  $100^\circ$ .

$\beta$ -Hydroxycinchoninic acid is converted by oxidation with potassium permanganate into pyridine-tricarboxylic acid,  $C_5H_2N(COOH)_3$ : hence it may be inferred that the hydroxyl-group in this acid, and in the  $\beta$ -quinophenol, and the  $SO_3H$ -group in the  $\beta$ -sulphonic acid, are situated, as in the corresponding  $\alpha$ -compounds, in the benzene-nucleus of the quinoline molecule (Abstr., 1881, 745).

$\beta$ -Hydroxycinchoninic acid is the fourth known hydroxyquinoline-carboxylic acid, inasmuch as Kretschy has shown (Abstr., 1881, 827), that kynuric acid is a compound of similar constitution;  $\beta$ -quinophenol is the third known hydroxyquinoline.

H. W.

**Cinchonidine.** By A. CLAUS and H. WELLER (*Ber.*, 14, 1921–1924).—In order to investigate the constitution of the haloïd and hydrocarbon derivatives of cinchonidine, the authors have examined their products of oxidation: for if the hydrocarbon residue is attached to the carbon-atom which serves for the production of quinoline-carboxylic acid, a dicarboxylic acid should be produced by its oxidation; but if the hydrocarbon residue is attached to a nitrogen-atom in that portion of the molecule which does not suffer disruptive oxidation, an alcoholic carboxylic acid should be formed; and finally, if the hydrocarbon grouping is in the other portion of the molecule, then quinolinemonocarboxylic acid should be produced.

By the oxidation of bromethylcinchonidine, quinoline monocarboxylic acid was formed identical with the acid obtained by the direct oxidation of cinchonidine.

Ethyl bromide combines easily with cinchonidine, but amyl bromide yields amyleinchonidine only when the two are heated together at  $210^{\circ}$  for some time. The *platinochloride* of amyl-cinchonidine forms a golden-yellow precipitate of composition  $C_{19}H_{21}(C_5H_{11})N_2O, H_2PtCl_6$ . The difficulty of combining amyl bromide with cinchonidine, as compared with the readiness with which amyl bromide combines with dimethylaniline, seems to the author to point to the formation of a hydrobromide of a tertiary amine, and not a tetrammonium bromide.

In conclusion, the author remarks that the existence of cinchonidine and homocinchonidine as two distinct chemical compounds has not been established, and that the difference in physical properties of these substances probably arises from the presence of impurities.

V. H. V.

**Cinchonidine and Homocinchonidine.** By O. HESSE (*Ber.*, 14, 1888—1890, and 1890—1895).—This paper is a personal discussion between the author and Skraup with regard to the two alkaloids cinchonidine and homocinchonidine (*Abstr.*, 1881, 291), in which the author arrives at the conclusion that Skraup's view (that the author's cinchonidine is impure homocinchonidine) is incorrect.

The author corrects an observation made in a former communication, that cinchonidine in sulphuric acid gives a blue fluorescent solution. This has subsequently been found to be due to the presence of about 2 per cent. of quinine.

In the second paper the distinctive characteristics of the two allied alkaloids, cinchonidine and homocinchonidine, are compared and contrasted. The former melts at  $200-201^{\circ}$ , the latter at  $205-206^{\circ}$ ; in alcohol and chloroform solution both have the same levorotatory power, but different when dissolved in acids (*Abstr.*, 1881, 292); the same relation holds good with the hydrochlorides of these bases.

Cinchonidine sulphate forms glistening prisms, which after a short time lose their brightness, with simultaneous absorption of 5 mols.  $H_2O$ ; whereas homocinchonidine sulphate forms needles, which, on keeping, shrivel up to an insignificant mass. The sulphates also differ in their solubility in water; at  $22^{\circ}$  the homocinchonidine sulphate is less soluble than the cinchonine sulphate; at  $30^{\circ}$  both salts are equally soluble; at a higher temperature homocinchonidine sulphate is more soluble; thus a solution of homocinchonidine sulphate saturated at  $50^{\circ}$  solidifies on cooling into a thick mass so compact that on turning over the vessel containing it, none of the mother-liquor falls out, which is not the case with cinchonidine sulphate. On oxidation with alkaline permanganate, both alkaloids yield the same cinchotenidine; but as the yield is different, it appears that the oxidation of the two alkaloids under the same conditions is also different. (In the rotatory power of cinchotenidine, the author has found (for  $p = 5$ ,  $t = 15$ ,  $l = 210$ )  $[\alpha]_D = -201.4$ ). For these reasons the author maintains that cinchonidine and homocinchonidine are not the same substance in different degrees of purity.

V. H. V.

**A New Cinchona Alkaloid.** By ARNAUD (*Compt. rend.*, 93, 593—595).—A new alkaloid, to which the author gives the name *cinchonamine*, exists in cinchona bark obtained from the province of Santander, Columbia. It occurs simultaneously with cinchonine, 100 parts of cinchonine being accompanied by 0.2 part of cinchonamine. In order to extract the latter, the bark is treated with milk of lime, and the mixture allowed to dry at the ordinary temperature. It is then treated with boiling alcohol. After distilling the alcoholic solution, the residue is dissolved in dilute hydrochloric acid. The hydrochloride of cinchonamine crystallises out, whilst that of cinchonine remains in solution. Cinchonamine is insoluble in cold water. It crystallises in brilliant anhydrous colourless prisms (m. p. 195°) from an alcoholic solution, and in fine needles when deposited from an ethereal solution. Its alcoholic solution (at 93°) is dextrorotatory  $[\alpha]_D = +117.9^\circ$ . Its salts are precipitated by alkalis. The hydrochloride,  $C_{19}H_{24}N_2O.HCl + H_2O$ , crystallises in prisms, scarcely soluble in cold water. The platinochloride,  $2(C_{19}H_{24}N_2O.HCl).PtCl_4$ , is a crystalline yellow powder, almost insoluble in pure water and in water containing hydrochloric acid. The author has also prepared the sulphate, nitrate, hydride, and acetate of the base. An acid solution of the sulphate is dextrorotatory  $[\alpha]_D = +45^\circ 5'$  at 16°.

J. I. W.

**Hyoscyne.** By A. LADENBURG (*Ber.*, 14, 1870—1872).—A continuation of the author's researches (*Abstr.*, 1881, 56). The hydride of hyoscyne,  $C_{17}H_{23}NO_3.HI + \frac{1}{2}H_2O$ , crystallises in small golden prisms of the monosymmetrical form, with axial ratio  $a : b : c = 0.9383 : 1 : 1.3565$  and  $\beta = 85.20$ . The hydrobromide crystallises in large colourless transparent prisms with axial ratio  $0.6005 : 1 : 0.4112$ . The hydride is levorotatory, and it is probable that the hydrobromide is also optically active.

V. H. V.

**The Lupine Alkaloids.** By G. BAUMERT (*Ber.*, 14, 1880—1882, and 1882—1884).—The author draws attention to the product which Liebscher obtained by the action of fuming hydrochloric acid on lupinine (*Ber. des Landwirthschaftliches Institutes der Universität Halle*, 2). Although Liebscher drew no inference as to the composition of the substance formed, on account of the unsatisfactory results of the analysis, the author considers that, adopting his formula for lupinine,  $C_{21}H_{40}N_2O_2$ , Liebscher's results indicate the existence of a base of composition  $C_{21}H_{38}N_2O$ .

On heating lupinine hydrochloride with phosphoric anhydride at 175°, dissolving the product in water, and precipitating with soda, a gold-coloured disagreeably smelling oil is obtained, which distils at about 215° in water-vapour with decomposition. This compound has properties similar to those of the substance examined by Liebscher. The platinochloride separates from aqueous solution in orange-red leaflets, of composition  $C_{21}H_{40}N_2O_5.H_2PtCl_6$ . On attempting to recrystallise this salt from hot water, the crystals lose water of crystallisation and their solubility is increased.

V. H. V.

**Berberonic Acid.** By H. FÜRTH (*Monatsh. Chem.*, **2**, 416—431).—This acid was described by Weidl (Abstr., 1879, 656), who considered it to be pyridine-tricarboxylic acid, and this view is confirmed by the author's researches. As at present no proof of the tribasic nature of the acid has been given, he has prepared the three potassium salts by adding the calculated quantities of potassium hydroxide to berberonic acid. The *normal* salt,  $C_8H_2K_3NO_6 + 4\frac{1}{2}H_2O$ , does not crystallise from water, but from 50 per cent. alcohol: it can be obtained in large hard brilliant prisms, of a yellowish tint; it is very deliquescent, readily soluble in water, insoluble in absolute alcohol, and has a neutral reaction. *Hydrodipotassic berberonate*,  $C_8H_3K_2NO_6 + 3H_2O$ , crystallises from its aqueous solution in brilliant white rhombic tables. It is little soluble in cold, readily in hot water, insoluble in alcohol. *Dihydrodipotassic berberonate*,  $C_8H_4KNO_6 + 1\frac{1}{2}H_2O$ , crystallises in hard brilliant needles, soluble in hot water, insoluble in alcohol.

Pure berberonic acid, when heated, turns red at  $215^\circ$ , and melts at  $243^\circ$ ; it yields a crystalline compound with hydrochloric acid. On heating berberonic acid to  $215^\circ$ , or the di-potassium salt to  $285^\circ$ , nicotinic acid and a small quantity of pyridine were obtained; whilst berberonic acid at temperatures above its melting point, or the monopotassium salt at  $275^\circ$ , gives isonicotinic acid and some pyridine. On heating berberonic acid with glacial acetic acid in sealed tubes at  $140^\circ$ , a new pyridinedicarboxylic acid was formed. The following table (p. 231) gives a comparison of the properties of this new acid with those of the five pyridinedicarboxylic acids previously known.

A. J. G.

**Products obtained by the Roasting of Coffee.** By O. BERNHEIMER (*Monatsh. Chem.*, **1**, 456—467).—Raw coffee beans (50 kg.) roasted in a revolving drum yielded a liquid distillate (5 l.), and a solid portion (680 g.) floating thereon. The uncondensable vapours contained carbonic anhydride, and, on passing them through dilute hydrochloric acid, a resinous body was deposited having the aspect of pyrrol-red.

**A. Liquid Distillate.**—The crude liquid distillate filtered from solid particles had a yellow colour and the fragrant odour of coffee. On agitating it with ether and evaporating the ethereal extract over the water-bath, a dark heavy oil was obtained, smelling like coffee, and yielding, on re-distillation, first a few drops of liquid having the odour of acetone, afterwards, for the most part, acetic acid and water. The thermometer then rose quickly to  $200^\circ$ , above which point there passed over an oil smelling like coffee, the temperature at the same time rising to  $300^\circ$ . Above this point there passed over a very small quantity of liquid which immediately solidified to a mass having the buttery aspect and rancid odour of the higher fatty acids. This portion, and the liquid which passed over from  $200^\circ$  to  $300^\circ$ , were neutralised with sodium carbonate, whereupon a thick dark-coloured oil was thrown down, which was separated from the supernatant liquid by means of a tap-funnel, and, washed with water rendered very slightly alkaline by potash.

The alkaline wash-waters contained no fatty acids, but, when acidulated with sulphuric acid and agitated with ether, they yielded a sub-

Melting point..	Lutidic acid.	Quinolic acid.	Böttger's acid.	Isochinomeric acid.	Chinomeric acid.	Dicarboxylic acid from berberonic acid.
Water .....	220°.	222—225°.	234—235.5°.	236°.	249—251° (258°).	263°.
{ Silver ni- trate  Lead ace- tate  Copper acetate  Ferrous sulphate {	Difficultly soluble in cold, readily in hot	Difficultly so- luble in cold, more readily on heating	Nearly insoluble in both hot and cold	Difficultly soluble even in hot	Insoluble in cold, nearly insoluble in hot.	Little soluble in cold, very readily in hot water.
	Gelatinous white precipitate	Flocculent ge- latinous pre- cipitate	Flocculent amor- phous precipi- tate	Pulverulent white precipitate	White distinctly crys- talline precipitate	Flocculent white pre- cipitate.
	White precipi- tate insoluble in water and in excess of the precipitant	.....	White crystalline precipitate in- soluble in boil- ing lead acetate	White crystalline pre- cipitate, partly so- luble in water, readily soluble in excess of the pre- cipitant	White flocculent pre- cipitate soluble in excess of the pre- cipitant	White flocculent pre- cipitate insoluble in water or in excess of the precipitant.
	Light blue indis- tinctly crystal- line precipitate	Light blue difficultly so- luble floccs	No precipitate even on boil- ing; a blue crystalline pre- cipitate from a concentrated solution of the ammonium salt	A light bluish-violet crystalline precipi- tate on continuous boiling	A precipitate in the cold soluble in slight excess of the pre- cipitant; on boiling, a green precipitate, becoming crystalline on slow cooling	At the boiling heat a light bluish-green flocculent precipitate which redissolves in the cold.
{ Water of crys- tallisation	Blood-red color- ation; after some time, a red precipi- tate	Reddish - yel- low color- ation	Yellowish - red coloration	Brownish-yellow co- loration	No reaction .....	No coloration.
	1 mol. ....	Anhydrous....	2 mols. ....	1 mol., or under cer- tain circumstances 1½ mols.	Anhydrous .....	Anhydrous.
A. J. G.						

Behaviour with



stance which, after evaporation of the ether, filled the liquid with a pulp of crystals, and, after precipitation, crystallised in colourless needles exhibiting the characters of quinol (m. p.  $171^{\circ}$ ; conversion into quinhydrone by the action of ferric chloride).

The oil above mentioned, designated by the author as *caffeol*, was dried over calcium chloride and fractionally distilled, the greater part passing over from  $195^{\circ}$  to  $197^{\circ}$ . The distillate smells very strongly of coffee, is apparently insoluble in cold water, but imparts to it the characteristic odour; slightly soluble in hot water, very slightly in aqueous potash, very easily in alcohol and ether, the alcoholic solution giving, with ferric chloride, a red coloration which does not disappear on addition of sodium carbonate. *Caffeol* does not solidify in a freezing mixture. By analysis it gave 69.57 and 69.77 per cent. carbon, 7.77 and 7.73 hydrogen, leading to the formula  $C_8H_{10}O_2$ , which requires 69.56 C and 7.25 H. Its vapour-density is by experiment 4.1, the formula requiring 4.7. *Caffeol* is violently oxidised by chromic acid mixture, without formation of any definite products. By fusion with potash, it yields salicylic acid. Respecting its constitution, see page 174.

The portion of the crude liquid distillate not taken up by ether, when concentrated over the water-bath, yielded groups of needle-shaped crystals, exhibiting the composition and properties of *caffeine*,  $C_8H_{10}N_4O_2$  (0.28 per cent. of the coffee). The mother-liquor was found to contain methylamine and trimethylamine.

*B. Solid Distillate.*—The black mass floating on the crude liquid distillate was found, by a preliminary examination, to consist of a mixture of the higher fatty acids. By saponification, and treatment of the product by Heintz's method of separation, this mixture yielded, as chief constituent, palmitic acid melting at  $60^{\circ}$ , and a very small quantity of another acid having a melting point a few degrees higher than that of lauric acid.

*Summary.*—From the preceding investigation, it appears that the chief products obtained by the roasting of coffee are palmitic acid, *caffeine*, *caffeol*, acetic acid, and carbonic anhydride; whilst, as secondary products, are obtained quinol, methylamine, pyrrol, and acetone (?). The fatty acids amount to 0.48 per cent. of the coffee used, the *caffeine* to 0.18, and the *caffeol* to 0.05 per cent. H. W.

**Reactions of Bile-pigments.** By ST. CAPRANICA (*Gazzetta*, 1881, 430).—The author, after reviewing the researches of Maly and Thudichum on the brominated derivatives of bilirubin, proceeds to describe three series of reactions which the bile-pigments exhibit with an alcoholic solution of bromine (5 per cent.), and with aqueous chloric and iodic acids (20 per cent.).

These reactions exhibit three stages of coloration: 1. Green; 2. Blue; 3. Violet; after which there occurs a change of colour to reddish-yellow, and, finally, decoloration. The reactions in question are obtained with all the bile-pigments dissolved in alcohol, ether, or chloroform. Some divergencies between the reactions with different solvents are, however, noticed, and these are shown to vary with the nature of the solvents themselves.

The spectroscopy of the solutions is also discussed, and the facts observed are arranged in a table, from which it appears that the green solutions do not exhibit any absorption-bands; whereas the blue solutions give one band in the red; the violet solutions two bands, one in the red, the other in the indigo; and, lastly, the red-yellow solutions give a single band in the blue. The bands exhibited by the coloured solutions obtained with the three reagents are always identical in position and intensity.

The first part of the memoir contains determinations showing the non-identity of the bile-pigments (positively asserted by some writers) with other pigments of the organism, especially with Virchow's hæmatoidin. The author then studies the allied pigments, viz., the lutein of the epithelium of the retina, hæmatoidin (hæmalutein), the yellow bodies of the ovary, and the pigments of the egg. Neither of these pigments was found to exhibit the reactions above mentioned with bromine, chloric acid, or iodic acid, whence it is inferred that they are essentially different from bilirubin.

The author has also studied the action of direct solar light on bilirubin, and finds that when solutions of this pigment in chloroform are exposed to light in sealed tubes, bilirubin is produced. On subsequently passing a current of air for several hours into solutions of bilirubin, neither green coloration nor decoloration was observed. Hence it is inferred that the action of light alone is sufficient to transform bilirubin into biliverdin, and that, under the conditions above mentioned, the air has no influence on the result. These phenomena serve to verify the non-identity of bilirubin with the colouring matters above mentioned, inasmuch as the latter, when exposed to light, are more or less quickly decolorised, but never turn green.

Lastly, the author has studied Maly's hydrobilirubin, which has been recognised as identical with many pigments of the organism, viz., the steriobilin of Vaulair and Masius, the urobilin of Jaffé, and, finally, the pigment which Hoppe-Seyler obtained by treating the colouring matter of blood with tin and hydrochloric acid. Hydrobilirubin does not give the above-mentioned reactions with bromine, chloric acid, &c.

The author's test for bile-pigments is more sensitive than that of Gmelin (limit found by the author for the action of bromine =  $\frac{1}{1000000}$  gram), and is very easy of execution.

The facts on which the author chiefly insists are the three series of reactions above described; the action of light on bilirubin, and the direct demonstration of the non-identity of bilirubin with hæmatoidin and other substances related thereto.

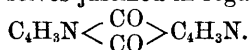
H. W.

**Some Derivatives of Pyrocoll.** By G. L. CIAMICIAN and L. DANESI (*Gazzetta*, 1881, 330—332).—This substance, discovered by Weidel and Ciamician (*Abstr.*, 1881, 295) amongst the products of the dry distillation of gelatin, is attacked by bromine at ordinary temperatures; but, to render the action complete, it is best to heat 1 part of pyrocoll and 2 parts bromine at  $120^{\circ}$  for about two hours in sealed tubes with a quantity of glacial acetic acid sufficient to dissolve the pyrocoll. On opening the tubes, a considerable quantity of hydro-

gen bromide escapes; and, on pouring the contents into a large quantity of water, a brominated compound separates in the form of a flocculent precipitate, which may be purified by dissolving it in glacial acetic acid at the boiling heat, filtering, treating the red-brown filtrate with animal charcoal, and pouring the resulting light-yellow liquid, after concentration, into a large quantity of water. The light-yellow precipitate thereby obtained is a mixture of two bromine-compounds which differ in their solubility in glacial acetic acid and in ether, but are best separated by sublimation, the one which is most soluble in ether subliming at a slightly elevated temperature, whereas the other requires a stronger heat. The former consists of *mono*-, the latter of *di*-bromopyrocoll.

*Monobromopyrocoll*,  $C_{10}H_5BrN_2O_2$ , forms nearly colourless scales, slightly yellow in mass, having a mother-of-pearl lustre, very soluble in ether and in acetic acid, and separating from the ethereal solution by slow evaporation, in small colourless prisms melting at  $190-192^\circ$ .

The formation of this compound shows that the molecule of pyrocoll contains 10 atoms of carbon, and from certain reactions of this body, which the authors hope to publish shortly, they consider themselves justified in regarding it as a quinone represented by the formula



H. W.

**On the Albuminoids in Oil-seeds.** By H. RITTHAUSEN (*J. pr. Chem.* [2], **24**, 257—273).—Hazel nuts contain albuminoids which can be removed by water, by salt solution, and by dilute potash. If the nuts are treated without removal of the skin, tannins interfere with the purity of the product, as also with the yield; but, if after being skinned and freed from fat, they are extracted with water, they yield a soluble albuminoid which is capable of precipitation by the addition of a few drops of sulphuric acid; this precipitate, after being washed with alcohol and ether and dried, is a white powder amounting to  $22\frac{1}{2}$  per cent. of the original dried matter; in the filtrate, after the removal of this substance, there still remains a portion precipitable by copper salts = 10.8 per cent.; and by treatment of the residues insoluble in water with potash, a further portion is removed = 14.81 per cent. The appearance of the albuminoid removed by potash solution is less dense than that obtained when water alone is employed, and is different as regards the quantity of carbon and sulphur present, but only the former product can be considered as pure. The amount of nitrogen present (18.7) is nearly the same as that found in the albuminoid of almonds; so that on all accounts these two albuminoids may be considered as identical, but not identical with that of lupines, castor-oil nuts, &c., which have more sulphur. This seems to be the only albuminoid present in hazel nuts, but sugars are present, as also an aromatic substance which is volatile with water-vapour.

*Walnuts*.—The skin of these nuts contains a considerable amount of iron-bluing tannin. From the skinned kernel potash extracts a white flocculent albuminoid containing 50.2 per cent. C, 18.2 per cent. N, and 0.76 per cent. S; so that the albuminoid in walnuts is the same as that in hazel nuts.

*Candlenuts*.—The presscake obtained after removal of the oil from the nuts contains 57 per cent. albuminoids, and is therefore largely used as a feeding-stuff. This presscake, after washing with ether, yields a glutinous mass, from which potash removes albuminoid = 46·3 per cent. which, under the microscope, appears to be a crystalloid. Water and salt solutions remove but a very small quantity from the glutinous mass above referred to. Conglutin, removable by lime-water, is present only to the amount of 4·5 per cent., so that the albuminoid in candlenuts consists for the most part of such as are poor in nitrogen, viz., 17·2 per cent.

The protein grains appear to be ill-formed crystalloids which, when moistened, are transparent, and contain 72·8 per cent. of albuminoids and 11·39 per cent. ash, consisting of 52·97  $P_2O_5$ , 20·33  $K_2O$ , &c.: a little sulphur, iron, and sodium, and the bases are in the condition of diphosphates.

The following is the composition of the protein grains of several nuts and seeds:—

	Para nuts.	Earth.	Candle.	Sunflower.	Castor-oil.
Ash .....	14·20	24·40	11·39	11·480	9·79
N .....	12·18	11·30	12·60	10·507	13·59
N × 5·5..	66·99	62·15	73·11	57·790	74·74

The albuminoids are different in composition and solubility.

*Radish seeds* contain conglutin, soluble in salt-water, to the amount of 19 per cent., and another albuminoid to the amount of 50 per cent. which is soluble in potash, and contains 16·9 per cent. N.

E. W. P.

**Some New Constituents of the Brain.** By G. PARCUS (*J. pr. Chem.* [2], **24**, 310—349).—The commencement of this paper is occupied by a recapitulation of the work done by various experimenters on the substances hitherto known as cerebrin, cerebrie acid, &c. As so much uncertainty seemed to exist concerning the composition, &c., of true cerebrin, as also of its sources, whether it be a decomposition-product of protagon or not, it was thought advisable to prepare large quantities of cerebrin and to examine it. The cerebrin was prepared by Müller's process (*Annalen*, **105**, 341), and purified by repeated crystallisations; cerebrin was obtained in a pure state, and two other compounds were found in the mother-liquors, to which the names homocerebrin and encephalin have been given. Repeated crystallisation of cerebrin in no way alters its composition, the pure substance containing 2 per cent. less nitrogen than is contained in that obtained by Müller. The analyses agree best with the formula  $C_{90}H_{160}N_2O_{15}$ , although  $C_{70}H_{140}N_2O_{13}$  and  $C_{76}H_{154}N_2O_{14}$  closely approximate. To represent the composition of homocerebrin, the formula  $C_{70}H_{136}N_2O_{12}$ ,  $C_{76}H_{152}N_2O_{13}$ , or  $C_{80}H_{158}N_2O_{14}$ , may be employed; but without further knowledge of the decomposition-products of either cerebrin or homocerebrin no more exact formula can as yet be given. Still between

the formulæ for cerebrin and those for homocerebrin, an evident connection exists, viz., that the one differs from the other by 1 mol.  $\text{H}_2\text{O}$ . But if the first formula for cerebrin be compared with the second for homocerebrin, it seems as if we had homologous substances to deal with, the difference being  $(\text{CH}_2)_6$ , and this is supported by the fact that dehydrating agents have no effect on cerebrin.

Enkephalin is represented by  $\text{C}_{102}\text{H}_{206}\text{N}_{14}\text{O}_{19}$ . The properties of cerebrin are fully described, the crystals appearing as globules under the microscope. Cerebrin is soluble in warm acetone, chloroform, benzene, &c.; it is not very hygroscopic, combines with bases: its solutions are neutral, and are not decomposed by long boiling with water, although it is completely destroyed by baryta-water. Boiled with hydrochloric acid for a long time it seems to give a sugar and a humus-like mass. The principal points therefore in which this cerebrin differs from that previously prepared are (1), the formation of a light yellow solution with concentrated sulphuric acid; (2), insolubility in hot ether; (3), small amount of swelling with hot water; (4), not being hygroscopic; (5), melting without decomposition; (6), but decomposing at a much higher temperature; (7), and the changes induced by long-continued boiling with baryta-water. Therefore Fremy's cerebric acid, obtained by extraction from the brain with hot ether, cannot be cerebrin; and Müller's cerebrin containing 4.6 per cent. N can only be considered as an impure substance. Otto's cerebrin and Köhler's myelomargarin may be decomposition-products of cerebrin, and of the substances obtained by Thudicum; only kersin approaches cerebrin in composition, and as homocerebrin and enkephalin are about identical with any of the other substances, stearonote, phrenosin, and cerebrin, the author considers that Thudicum must have been examining impure specimens of cerebrin. Concerning the properties of homocerebrin, it is soluble in all the solvents of cerebrin as well as in hot ether, swells up in hot water, but is not decomposed by boiling. On boiling it with hydrochloric acid, a reducing solution is formed; baryta-water decomposes it after long boiling; it is not hygroscopic, it is neutral in solution, and crystallises in long white needles, melts without decomposition, but at  $155^\circ$  forms a brown syrup. Whilst 1 part cerebrin is soluble in 12,200 parts alcohol, homocerebrin dissolves in 1,934 parts, affording a means of separation. Cerebrin and homocerebrin cannot be decomposition-products of protagon, as stated by others, but exist as such in the brain. Enkephalin can be separated from homocerebrin by means of acetone, in which both are less soluble than in alcohol, and with which the former forms a glutinous mass. Pure enkephalin occurs in small plates, which when separated rapidly from the acetone solution assume a granular condition. It begins to decompose at  $125^\circ$ , and is converted into a brown liquid at  $150^\circ$ . Hot water causes enkephalin to swell to a glutinous mass, whereby it may be readily distinguished from the other two substances; its origin is not certain, but it is believed to be formed from cerebrin or homocerebrin. The final results of the investigation are, that nitrogen is not removed by alcohol from cerebrin, and that the cerebrins previously described consist of mixtures of the three substances above mentioned.

E. W. P.

## Physiological Chemistry.

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**Digestion of Celluloses.** By HOFMEISTER (*Bied. Centr.*, 1881, 669—674).—To determine in what part of the digestive organs and by what fluid cellulose was digested in ruminants, freshly mown grass, enclosed in a suitable apparatus, was introduced into the rumen of a sheep, and allowed to remain there for three days; it was then found that 78·4 per cent. of the 21·6 per cent. of fibre present in the grass had been removed. Grass was also submitted to the solvent action of liquid manure, in case the solution were effected by bacteria, &c., and also to the action of gastric juice taken from a sheep's stomach; it was then found that whereas the gastric juice had dissolved 78·8 per cent., the liquid manure had removed only 3·5 per cent. of the fibre. As regards the total dry matter, both liquids had removed a portion. To determine the action of other fluids, glycerol was added to gastric juice, and this mixture was allowed to act on grass, as was also some of the original gastric juice. It was found that the presence of glycerol prevented the formation of bacteria, &c., which were to be found in the plain fluid, but both liquids dissolved fibre and dry matter, the former only to a small extent, and in neither were the amounts dissolved equal to those in the first experiments. It was therefore decided to add to the gastric juice, saliva from the various glands, and to observe the result. Of 100 parts dry matter, there were absorbed by mixed saliva 70·4, by parotid fluid 41·5, by submaxillary fluid 49·2 parts; and of 100 parts fibre, mixed saliva dissolved 80·4, parotid fluid 40·8, and submaxillary 18·1 parts. Sublingual fluid was also employed, but only 41·7 per cent. of the dry matter, and 16·4 per cent. of the fibre was dissolved. The fibre of hay is also soluble in gastric juice, and the amount that is dissolved is dependent on the quantity of available fluid. In the horse, the saliva seems to have no action on cellulose. E. W. P.

**Comparative Experiments on the Digestion of Two Kinds of Clover Hay by the Horse and Sheep.** By E. WOLFF and others (*Bied. Centr.*, 1881, 682—684).—Previous researches with lucerne hay showed that, as regards the albuminoids and extractive matter, the digestion of the horse and sheep were alike, and that the difference between the digestion of the fibre in the sheep and in the horse was not so great as was found when meadow hay was employed. Even when very fibrous lucerne was given as fodder, no difference in digestive capabilities could be found. It was, therefore, determined to repeat the experiments, using two sorts of clover hay, common red clover, and a kind from East Prussia, both of which consisted principally of stems, the leaves from various causes having been lost. The only differences observable in the digestive coefficients of these fodders, as compared with that of the other hays, is to be found in the digestion of the crude fibre and extractive matter. The mean differences for crude fibre are in the lucerne, clover, and meadow hay, 9·44, 14·8,

and 20.5 respectively; of the nine kinds of meadow hay employed, not one gave a difference of less than 15, while one kind even amounted to 28. To account for this great variation, the percentage of fibre present is insufficient. As regards "extractive," a mean difference of 7.6 per cent. was found with meadow hay, the quantities fluctuating between 4.1—10.7 in favour of the sheep; on the other hand, when clover and lucerne are eaten, there seems to be no difference in its digestion by either animal.

E. W. P.

**Feeding Milch Cows with Grass and Lucerne.** By J. SAMEK (*Bied. Centr.*, 1881, 713).—The experiments were instituted to determine whether dry or green fodder exerted the greater influence on the milk secretion. The quantity of milk increased with the green food, but the quantity of cream diminished. In another set of experiments it was found that green lucerne greatly increased the secretion and the sp. gr. of milk, as also the quantity of cream.

E. W. P.

**Researches on the Formation of Fat in Animals.** By F. SOXHLET (*Bied. Centr.*, 1881, 674—679).—The experiments were made on pigs, and the conclusions drawn are that the decomposition of the albuminoids in the food is insufficient to account for all the fat formed, as there was 5—6 times more fat formed than could be produced by the albuminoids given, and as the food (rice) was poor in fat, it is clear that the carbohydrates were chiefly instrumental in its production. The researches also show that it is advisable to feed with food containing but little fat, and having a nutrient ratio of 1 : 11. The unsatisfactory results obtained by feeding with potatoes, which are considered to have the same nutrient ratio as rice, is due to the fact that their nutrient ratio is really 1 : 20.

E. W. P.

**The Hydration Processes Occurring during the Formation of Peptones from Albumin.** By A. DANILEWSKY (*Bied. Centr.*, 1881, 712).—Peptones dried above 100° lose water and become insoluble, but remain unaltered at 98—100°. Albumin under the influence of pepsin assumes water, forming peptones containing 5.72—6.77 per cent. of water.

E. W. P.

**Elimination of Free Nitrogen from the Body.** By M. PETTENKOFER and C. VOIT (*Bied. Centr.*, 1881, 640—682).—The author considers that the discovery by Seegen and Nowak (*Abstr.*, 1880, 272) of the elimination of free nitrogen from the body is incorrect, and that the nitrogen observed was due to errors in experimenting; the separating liquid in the gasometer, although covered by a layer of oil, was insufficient to prevent the entrance of air. Potassium chlorate and manganese dioxide do not yield pure oxygen, but oxygen mixed with nitrogen; other sources of error are also mentioned.

E. W. P.

**Elimination of Urea.** By H. OPPENHEIM and J. MEYER (*Bied. Centr.*, 1881, 665—667).—Under normal conditions the quantity of nitrogen eliminated in a day amounted to 16.2 grams, of which 1.1 appeared in the fæces. Of urea there appeared to be eliminated 34.8

grams, and the hourly quantity was dependent on the time elapsing after consumption of nitrogenous food; during the first four hours, after a midday meal, the quantity was 0·24 gram in excess of the mean quantity, and during the night the quantity sank below the average. Fasting lowered the quantity by 10—11 grams, whereas excessive consumption of water (4 litres) raised the amount by 5 grams. Consumption of coffee and perspiration artificially produced appeared to have no effect, whilst 2 grams of quinine, taken in 24 hours, raised the elimination by 4 grams. As a rule, muscular exertion causes no increase, but under certain circumstances, an increase has been observed when muscular action is accompanied with dispnœa. According to Fraenkel, dispnœa causes an increased decomposition of albumin, therefore it appeared probable that in a number of experiments it would produce some effect. The accuracy of this conclusion was proved by experiment, when it was found that climbing caused an elimination of 39·78 grams urea (pulse 140—150). Labour, dispnœa supervening, had the same result. Patients afflicted with phthisis eliminate more nitrogen as urea than is present in the food consumed.

J. Mayer does not find that an increase of nitrogen accompanies an increased secretion of urine.

E. W. P.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Proportion of Free Fatty Acids in Vegetable and Animal Fats.** By V. RECHENBERG (*Ber.*, 14, 2216—2218).—According to the researches of F. Hofmann, human fat and the fat of swine and oxen, are neutral fats containing but a small and variable quantity of free fatty acid; whilst it follows from the results of König and others, by the determination of the proportion of glycerol present, that vegetable fats contain a relatively large proportion of free fatty acid.

As the author considers that exact conclusions cannot be drawn when this method of analysis is used, he has made a series of determinations of the quantities of free fatty acid in seeds of various ages, and various degrees of ripeness. From an examination of rape seed, linseed, poppy seed, and others, the author finds that the unripe seeds contain a larger quantity of free fatty acid than the ripe seed, even though the seed be separated from the plant, and that a chemical change goes on whereby the proportion of free fatty acid is diminished, whilst that of the neutral fat is increased. After the germination of the seed has commenced, a reverse change takes place, and the proportion of free fatty acid is increased. But in all cases examined, the fats of oil seeds resemble those of animal origin in being neutral fats, and containing only traces of free volatile and non-volatile fatty acids.

V. H. V.

**Chemical Composition of Human Fat at Different Ages.** By L. LANGER (*Monatsh. Chem.*, **2**, 382—397).—Considerable difference exists in the chemical and physical characters of the fat of a newly born infant and of an adult. The fatty tissues of the adult are clear yellow to brownish in colour and very soft; small oil globules are visible, and microscopic examination shows one or more oil globules in every cell, whilst but few of the cells contain fat crystals.

In the infant body the fatty tissues have a firmer and harder consistence, there are no oil globules, and nearly every cell contains fat crystals. Infant fat forms a homogeneous, white, solid, tallow-like mass, and melts at 45°. Adult fat, on standing in a warm room, separates into two layers; the lighter and more considerable is a transparent yellow liquid, which solidifies below 0°; the lower layer is a granular crystalline mass melting at 36°. Infant fat contains more stearic and palmitic acids, and less oleic acid than adult fat, the relative amounts being given in the following table:—

	Infant.	Adult.
Oleic acid.....	67.75	89.80
Palmitic acid .....	28.97	8.16
Stearic acid.....	3.28	2.04

Of the volatile fatty acids only the glycerides of butyric and caproic acids could be detected, infant fat containing considerably more than adult fat. Cetyl alcohol was not detected in either case.

A. J. G.

**Formation of Phenol, Indole, and Skatole in the Intestines of Herbivora.** By H. TAPPEINER (*Ber.*, **14**, 2382—2384).—Phenol and skatole are found in the first stomach of cattle. Indole occurs in the large and small intestines.

The small intestines of the horse also contain indole. The cæcum contains a considerable quantity of indole, and the colon skatole. Hence it appears that there are two kinds of marsh-gas fermentation, viz., an acid fermentation producing skatole, and an alkaline fermentation producing indole.

W. C. W.

**Intestinal Gases of Herbivora.** By H. TAPPEINER (*Ber.*, **14**, 2375—2381).—The author has analysed the gases contained in different portions of the intestines of sheep, cattle, goats, and horses, and also the gases obtained by fermenting the contents of the intestines.

The following results were obtained:—

*Intestinal Gases of Cattle fed on Hay.*

I. Collected directly. II. Obtained by Fermentation.

	First Stomach.	Small intestines.			Large intestine.	Rectum.
		Beginning.	Middle.	End.		
I.						
CO <sub>2</sub> } ....	65·27	17·69	—	—	36·35	14·46
H <sub>2</sub> S } .....	0·19	3·96	—	—	2·29	—
H.....	30·55	49·15	—	—	35·21	44·23
CH <sub>4</sub> .....	3·99	29·96	—	—	23·14	41·31
N.....						
II.						
CO <sub>2</sub> } ....	75·47	62·06	81·65	92·33	80·84	—
H <sub>2</sub> S } .....	0·07	37·64	17·60	0·01	—	—
H.....	23·27	0·41	—	6·59	17·25	—
CH <sub>4</sub> .....	1·31	—	0·71	1·20	1·97	—
N.....						

*Intestinal Gases of Horse fed on Hay.*

	Stomach.	Small intestines.		Cæcum.	Colon.	Rectum.
		Beginning.	End.			
I.						
CO <sub>2</sub> } ....	75·20	42·70	15·65	85·47	55·18	29·19
H <sub>2</sub> S } .....	0·23	—	—	—	—	—
O.....	14·56	19·38	24·06	2·33	1·69	0·83
H.....	—	—	—	11·16	32·73	56·62
CH <sub>4</sub> .....	9·99	37·44	59·62	0·90	9·99	13·44
N.....						
II.						
CO <sub>2</sub> } ....	—	—	80·60	85·40	70·49	—
H <sub>2</sub> S } .....	—	—	15·65	0·50	—	—
H.....	—	—	0·09	13·40	26·08	—
CH <sub>4</sub> .....	—	—	3·66	1·20	3·43	—
N.....						

The gases in the first stomach of ruminants consist chiefly of carbonic anhydride and marsh-gas in the proportion of 2 to 1. In the small intestine hydrogen takes the place of marsh-gas.

The gases generated in the large intestine are the same as those formed in the stomach, but the fermentation which takes place in the latter gives rise to acid products, whilst the contents of the large intestine yield an alkaline liquid on fermentation.

In the stomach of the horse, a considerable quantity of hydrogen is

formed. No marsh-gas is produced in the small intestines. In the colon of the horse an acid fermentation takes place.

The composition of the gaseous mixture is not influenced by addition of oats to the fodder. W. C. W.

**Theory of the Physiological Action of Arsenic.** By C. BINZ and H. SCHULZ (*Ber.*, **14**, 2400—2403).—The authors criticise the remarks which Dogiel (*Pflüger's Archiv.*, **24**, 1880) and Filehne (*Virchow's Archiv. Patho. Anatomie of Physiologie*, **83**, 1881) have made on their researches (*Ber.*, **12**, 2199). They also point out that arsenic acid is more rapidly reduced to arsenious acid by the liver than by albumin, and more rapidly by putrid than by fresh fibrin. W. C. W.

**An Ancient Ostrich Egg.** By BALLAND (*Compt. rend.*, **93**, 550—551).—An ostrich egg was found in 1878 in a subterranean vault, together with some bronze coins of the time of Antoninus. The author has made analyses of the shell, and also of that of a recent one obtained from South Africa. He finds the thickness (2 mm.) the same. The analyses are as follows:—

	Ancient.	Recent.
Sp. gr. at 20° C. ....	2.525	2.514
CaCO <sub>3</sub> .....	94.14	91.44
MgCO <sub>3</sub> .....	0.69	2.03
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> .....	1.82	0.70
Animal matter .....	3.05	4.92
Moisture .....	0.15	0.73
Loss .....	0.15	0.18
	100.00	100.00

J. I. W.

**Fixation of Atmospheric Ammonia by Plants.** By T. SCHLOESSING (*Ann. Chim. Phys.* [5], **24**, 284—288).—The author discusses the theories which have been advanced to account for the manner in which the amount of ammonia in the atmosphere is maintained. He specially adverts to that originated by Déhéraïn, according to which the vegetable world loses more combined nitrogen than it receives, and makes up its deficit by a direct absorption of gaseous nitrogen. He has repeated most of the experiments which were made by Déhéraïn, and fails to find evidence that this is the case. J. I. W.

**Loss of Starch occasioned by the Sprouting of Potatoes.** By E. KRAMER (*Bied. Centr.*, 1881, 717).—Potatoes which had sprouted in a dry and warm place were found to have lost starch. Tubers were examined, of which the sprouts were 1—2, 2—3, 3—4 cm. long, and the loss on 100 starch was found to be 3.18 per cent., 5.26 per cent., and 9.88 per cent. respectively. E. W. P.

**Development of Heat during Germination.** By G. BONNIER (*Bied. Centr.*, 1881, 716).—Seeds of agricultural plants have been found to develop 0—120 heat-units, the figure varying with the species. E. W. P.

**Loss of Water from Kidney Beans when Ripening.** By H. BRIEM (*Bied. Centr.*, 1881, 714).—The beans and pods lose their water in approximately the same ratio, although when young the relative weight of the beans to the pods is as 2·6 : 97·4, and when ripe, as 75 : 25 : both increase in absolute weight up to a certain date, after which no further increase is experienced, although loss of water takes place.  
E. W. P.

**Hydantoïn in Plants.** By E. SCHULZE and J. BARBIERI (*Ber.*, 14, 1834).—Besides the bodies obtained from *Platanus orientalis*, already described (*Abstr.*, 1881, 1061), the authors have obtained hydantoïn (m. p. 216°).  
P. P. B.

**Distribution of Myronic Acid in the Seed of Brassica Napus and B. Rapa.** By H. RITTHAUSEN (*J. pr. Chem.* [2], 24, 273—275).—Specimens of yellow and brown Indian rape seed, which are employed in the preparation of rape cake, were found to produce allyl thiocyanate when treated with water; yellow and white mustard do not produce allyl thiocyanate, but rather acrinyl thiocyanate,  $C_7H_7ONCS$ , whose odour is somewhat different; therefore, it was to be concluded that the seed under examination was not that of *Sinapis alba*. When the seeds were planted and had grown up, it was found that they were those of turnip. It is remarkable that so much myronic acid should be present in these seeds, and a cake in which such seeds occurred might readily be condemned as containing mustard seed. Russian and German rape cakes were not found to produce a trace of mustard oil with water, the odour which is produced being due to other sulphur compounds.  
E. W. P.

**Aldehyde-like Substances in the Cells of Plants containing Chlorophyll.** By J. REINKE (*Ber.*, 14, 2144—2150).—On distilling the juice expressed from the plants, and previously neutralised with sodium carbonate, substances pass over differing in their volatility but all reducing Fehling's solution, ammoniacal and even neutral silver salts. That they exist ready formed in the juices and do not depend on the decomposition of the albuminoid bodies or of the chlorophyll, was shown by the fact that some juices, after removal of these bodies, reduced silver salts. They do not exist in the unopened buds; therefore, it is probable that their formation depends on the action of sunlight. On account of the very strong reducing power, the author thinks that the active body is formaldehyde, which might be produced in this way: When the carbonic anhydride is absorbed by the plant, carbonic acid,  $CO_3H_2$ , is formed, and this, under the influence of sunlight, is reduced to formaldehyde,  $CO_3H_2 = O_2 + COH_2$ . He has not examined it chemically, but bases his opinions on the statements and work of Hoffmann and of Baeyer. Plants in which chlorophyll is absent do not contain this body.  
D. A. L.

**Cultivation of some Kinds of French Sugar-beet.** By A. NORD (*Bied. Centr.*, 1881, 697).—Five kinds of French sugar-beet and native sorts were grown with Chili saltpetre, ammonium superphos-

phate, and Baker Island guano. All the French sorts were found to be less hardy than the German, more rotten roots being found among them. In all cases the small roots gave the highest percentage of sugar in the juice.

E. W. P.

**Sugar-beet Culture in Vaucluse.** By P. PICHARD (*Bied. Centr.*, 1881, 699).—Comparative experiments on the growing of sugar-beet of different kinds. Figures are given which show the great difference in the amount of sugar present in roots of various sizes.

E. W. P.

**Bertel's Method of Sugar-beet Growing.** By G. MAREK (*Bied. Centr.*, 1881, 695—697).—Chiefly an agricultural paper, giving an account of an improved method of cultivation and implements recommended. By the new method, a larger yield of roots is obtained; also a larger amount of dry matter, and a juice of higher sp. gr. and polarisation than can be obtained by the old methods.

E. W. P.

**Application of Knop's Method to Danish Soils.** By C. F. A. TUXEN (*Bied. Centr.*, 1881, 649—651).—The result of the examination by Knop's method of nine different soils showed two soils nearly identical in composition, there being a deficit of humus and carbonates in the one which had received no manure for years, and therefore was apparently unfertile; still addition of manure would cause it to be as good as the other soil. "Red earth" and heaths, by reason of the excess of humus and ferrous oxide, were unfertile. The absorptive capacity of a soil for ammonia is a good indicator of its value, excepting "red earth" and heath land, which owe their high absorptive power to the large amount of humic acid present.

E. W. P.

**Peat, and Manures Prepared with it.** By R. ALBERTI (*Bied. Centr.*, 1881, 711).—Peat containing 0.49 per cent. N, and 1.33 per cent. ash, may be mixed with night soil, when a manure containing 2.3 per cent. ash, 0.78 per cent. N, 0.22 per cent.  $P_2O_5$ , and 0.28 per cent.  $K_2O$  is obtained. Such a mixture is more valuable than ordinary stable manure, is odourless, and can be easily applied to the land.

E. W. P.

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### Analytical Chemistry.

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**An Improved Form of Drying Apparatus.** By E. SEELIG (*Ber.*, **14**, 1814—1816).—This is a description of an air-bath of an improved form, with a gas regulator. P. P. B.

**Determination of Nitrous Oxide.** By G. LUNGE (*Ber.*, **14**, 2188—2196).—The author draws attention to the desirability of an exact method for the determination of nitrous oxide in gas analysis,

and to the unsatisfactory results obtained by the methods in use. Nitrous oxide is generally estimated after most of the other gases are removed by absorbents, but the substances used for the purpose, alkaline pyrogallate, ferrous sulphate, potash and concentrated sulphuric acid absorb considerable quantities of the nitrous oxide, and the author quotes experiments to show the errors which may thus arise. On exploding nitrous oxide with detonating gas or hydrogen, subsidiary reactions take place, which nullify the results; and on passing the gas over red-hot palladium-foil it is not completely decomposed into oxygen and nitrogen; finally, the method proposed by Winkler to pass the gas, together with excess of hydrogen, over red-hot finely divided platinum or palladium asbestos, and to estimate the ammonia formed by a volumetric analysis, yields doubtful results. The author finds that absolute alcohol, boiled until it is free from air, completely absorbs nitrous oxide; and a mixture of this gas with nitrogen can be analysed by Bunsen's absorptiometer. The great solubility of nitrous oxide in absolute alcohol can also be used to separate it from admixture with other gases, due allowance being made in the calculations for the solubility of other gases, and the tension of the vapour of alcohol.

The author gives a description of modified forms of gas pipettes and eudiometers, which cannot be rendered intelligible without the accompanying illustrations.

V. H. V.

**Detection of Boric Acid, Silica, and certain Metals by Means of the Microscope.** By H. REINSCH (*Ber.*, 14, 2325—2331).—The sulphates of aluminium, glucinum, potassium, sodium, lithium, ammonium, copper, manganese, cadmium, uranium, mercury, and silver crystallise from dilute solutions (4 or 2 per cent.) in characteristic forms, which can be easily recognised under the microscope. As the form of the crystals depends on the strength of the solution, a dilute solution of known strength must always be employed. Silica, aluminium, calcium, magnesium, and iron (ferrous) can be detected by examining the precipitate produced by the addition of one drop of a 1 per cent. solution of sodium bicarbonate to a 2 per cent. solution of any of the soluble salts of these elements. Boric acid is recognised by the change which the free acid undergoes when mixed with a dilute solution of sodium bicarbonate.

W. C. W.

**A Shortened Method of Soil Analysis.** By F. FARSKY (*Bied. Centr.*, 1881, 711).—The author treats the soil with hydrochloric, sulphuric, and hydrofluoric acids, allows the solutions to crystallise, and then examines them qualitatively and quantitatively under the microscope. It is hoped that this method may in time be extensively employed.

E. W. P.

**Testing Urine for Phenol by the Pine-wood Reaction.** By T. and D. TOMMASI (*Ber.*, 14, 1834—1835).—The authors recommend the following method of procedure:—20—25 c.c. of the urine are shaken out with ether, and the ethereal solution is poured on a chip of pine-wood, by which it is absorbed. The wood is then dipped into a



solution of hydrochloric acid containing a little potassium chlorate (50 c.c. hydrochloric acid, 50 c.c. distilled water, and 0.2 gram of potassium chlorate). The piece of wood, after removal from the hydrochloric acid, is exposed to direct sunlight, and in five minutes the blue coloration will appear if phenol be present. Pine-wood dipped into hydrochloric acid alone, and exposed to sunlight, becomes green, but this coloration is prevented if potassium chlorate is added to the hydrochloric acid. The above reaction serves to discover 1 part of phenol in 6,000 of water. The blue produced fades on exposure to sunlight.

F. P. B.

**A Ureometer.** By M. DE THIERRY (*Compt. rend.*, **93**, 520).—The apparatus devised by the author presents the following advantages over those in ordinary use. It allows the operator to work on a sufficient quantity of water to ensure an accurate result being obtained. The apparatus can be agitated during the experiment, and is easily portable.

J. I. W.

**Detection of Poisoning by Hydrocyanic Acid after a long Time.** By E. REICHARDT (*Arch. Pharm.* [3], **19**, 204—211).—The author succeeded in detecting hydrocyanic acid two months after death in a case of undoubted poisoning. He succeeded with the guaiacum copper test, and with the Prussian-blue test on the distillate from the organs previously acidified with tartaric acid, ferrocyanides and thiocyanates being previously proved to be absent. No definite results could be obtained from the urine.

F. L. T.

**Ptomaines.** By T. HUSEMANN (*Arch. Pharm.* [3], **19**, 187—204).—In an Italian criminal prosecution, F. Ciotto, who made the investigation of the corpse, gave as his opinion that “there was a body present which gave reactions corresponding with those of strychnine, and therefore probably was strychnine.” F. Selmi, for the defence, subjects the chemical evidence to minute criticism, pointing out several instances in which the reactions of the body present differ from those of strychnine, and considers the compound to be a ptomaine, with which opinion the author agrees.

F. L. T.

**Estimation of the Alkaloids in Cinchona-bark.** By PROLLIUS (*Arch. Pharm.* [3], **19**, 85—87).—Instead of employing lime, as is usual, to liberate the alkaloids from their compounds and to decolorise them at the same time, the author liberates them by ammonia, employing lime merely for the purpose of subsequent decolorisation. He obtains a wine-red solution by vigorously shaking up a mixture of 30 parts of alcohol, 10 of chloroform, 2 of ammonia solution, and 5 of powdered cinchona-bark. This solution decanted after several hours, is immediately decolorised by the addition of 5 parts of finely pulverised slaked lime. On evaporating to obtain the total alkaloids, the quinine is left as a varnish, the other alkaloids separating in the crystalline state. When the amount of quinine and the allied alkaloids soluble in ether is alone required, the process is still simpler, decolorisation not being requisite. The author acts on 3 parts of the

powdered bark for several hours with 30 parts of a mixture of 88 parts of ether, 4 of ammonia solution, and 8 of alcohol, the alcohol being merely added to mix the ammonia with the ether. All the alkaloids soluble in ether are completely dissolved, and the solution can be decanted clear without filtration being necessary. To 20 parts of this solution (= 2 parts of bark) five or six drops of dilute sulphuric acid are added, and on being left for a time the alkaloids are deposited as a thick fluid solution on the bottom of the glass, from which the ether can readily be poured off: the latter still retains a small portion of the alkaloid solution, which is washed out first with 2 and then with 1 part of water, these solutions being mixed with the one that separates first. The alkaloids are precipitated from the united solutions by ammonia, the alcohol being previously removed by heat.

The alkaloids extracted from the cinchona-bark by the mixture of ether, alcohol, and ammonia, can be separated from this solution as crystalline sulphates by shaking the solution with water several times so as to remove all the ammonia, and then adding just as much sulphuric acid as is required to neutralise the alkaloids. The crystals then separate, but redissolve on the addition of a drop too much acid. The above process of precipitating the alkaloids by ammonia is, however, more certain and accurate.

F. L. T.

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## Technical Chemistry.

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**"Tripolith."** By T. PETERSEN (*Ber.*, 14, 2361—2364).—The author finds that "Tripolith," which has been advocated as a material for building purposes, and as a substitute for plaster of Paris for casts and mouldings, is a mixture of plaster of Paris and 11 per cent. of coal or coke. It does not appear to possess any special advantages over ordinary plaster of Paris. W. C. W.

**Use of the Ferment Eurotium Oryzæ in Japan.** By LIEBSCHER (*Bied. Centr.*, 1881, 707).—This ferment, which is employed in the manufacture of Saki, not only causes the formation of alcohol, but also plays the same part as malt. It is to be hoped that in time it will be introduced into Europe, so that a more concentrated mash may be used than that now employed. E. W. P.

**Decorating Mirrors and Metallic Surfaces by the aid of Photography.** By LECLÈRE (*Chem. Centr.*, 1881, 448).—The silvered glass plate is well cleansed and covered with a layer of asphalt. The drawing or engraving to be reproduced is rendered transparent, and the dry asphalte layer under the transparent drawing is exposed to the action of light in a printing press. On subsequently washing the plate with turpentine or any other solvent for asphalt, the drawing

appears white on a dark ground, and all that is necessary is to remove the layer of silver with an acid, in order to obtain the picture on the plate. This is then painted with an oil colour, or gilded if required.

D. B.

**Utilisation of Residues.** By LADUREAU (*Ann. Agronomiques*, 6, 395—396).—In the north of France, the waste from woollen and mixed-stuff factories is heated in a close vessel to 300°. The wool blackens and becomes to a great extent soluble in water, whilst the cellulose is unaffected. By washing the product, vegetable fibre for paper manufacture is obtained, and a black mass containing about 30 per cent. of water and 10 per cent. organic nitrogen.

J. M. H. M.

**Utilisation of Sewage.** By LADUREAU (*Ann. Agronomiques*, 6, 396—397).—The sewage of Roubaix and Tourcoing contains much soap and oil, arising from the woollen factories. The compact soil of the district does not allow of its purification by filtration, and when distributed over the land it leaves a surface deposit which rapidly renders the soil sterile. The author has obtained good results in attempting its chemical purification with a mixture of lime and clay. At Rheims, irrigation and chemical treatment are both employed.

J. M. H. M.

**Analysis of Liebig's Extract of Meat and an Imitation of it.** By C. ESTCOURT (*Analyst*, 6, 201—202).—The chief differences between the genuine extract and the imitation, which is probably made from horse-flesh, are the excess of sodium chloride and the deficiency of phosphoric acid shown by the latter.

	Imitation.	Genuine.
Total solids.....	12·0	88·0
Water .....	18·0	12·0
Fat .....	1·0	—
Total ash.....	23·10	21·31
Ash, insoluble in water.....	1·32	1·48
Sodium chloride.....	14·21	8·12
P <sub>2</sub> O <sub>5</sub> , insoluble phosphates .....	1·765	4·627
H <sub>2</sub> SO <sub>4</sub> „ sulphates .....	0·451	0·606
Alkalinity of ash, expressed as NaHO..	2·401	2·160

L. T. O'S.

**Preparation of Black Chalk.** By S. MIERZINSKI (*Chem. Centr.*, 1881, 447).—The author uses ordinary lamp-black, which he proposes to press strongly and heat in closed vessels until the evolution of fumes ceases.

D. B.

**Improved Mode of preparing Violet Syrup.** By C. BERNBECK (*Chem. Centr.*, 1881, 448).—100 grams of the flowers of the violet are macerated with 50 grams of alcohol. The mixture is digested for six to eight hours, after which it is pressed, and the liquid made up to 100 grams with water. It is then filtered and mixed with 9 parts of syrup of sp. gr. of 1·36.

D. B.

## General and Physical Chemistry.

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**New Method of Spectrum Observation.** By J. N. LOCKYER (*Proc. Roy. Soc.*, 30, 22—31).—A continuation of the author's experiments on the dependence of the lines present in the spectra of the metals and their salts on the temperature at which volatilisation takes place. The phenomena observed are comparable with those which occur in the process of fractional distillation. At each heat-level, lines are produced due to particular vibrations of molecular groupings, of which some are produced with difficulty, whilst others represent the fading out of molecular groupings produced at a lower heat-level. In order to gain fresh evidence in support of these views, the author had made a comparative set of observations of the spectra produced in the Bunsen burner—firstly, by the flame only, secondly, by the passage of a strong electric spark through the flame. The results obtained by this method of observation solve some of the difficulties which arise in a comparison of the flame with the solar spectra. Thus, for instance, the flame spectrum of sodium gives the line D identical with a Fraunhofer line, whilst the flame spectra of lithium and potassium give red lines which have no representatives among the Fraunhofer lines. From the similarity of the flame and solar spectra of sodium, it appears that sodium is a body easily broken up, and the flame has effected this dissociation process as completely as the heat of the sun. If this be so, there should be no marked difference between the flame spectrum of sodium and that produced by the passage of the electric spark through the flame. Experiment largely confirmed this deduction. On the introduction of metallic sodium into the lower part of the flame, there appeared in the spectrum, besides the line D, the green lines and flutings observed by Roscoe and Schuster; on the passage of the spark, the double red line and the blue line appeared. On the other hand, the dissimilarity of the flame and solar spectra of lithium and potassium points to the conclusion that these elements resist decomposition: this was also confirmed by experiment, the passage of the spark in the flame during volatilisation of lithium chloride brought out the yellow and blue lines, which are reversed by the solar atmosphere. Similar results were obtained in the case of potassium, the lines corresponding with the Fraunhofer lines brightening up on the passage of the spark. So also in the flame spectrum of magnesium: a green triplet  $\lambda$  5209·8,  $b_1$  and  $b_2$ , and a blue line,  $\lambda$  4570·3, appear, but the passage of the spark causes  $\lambda$  5209·8 and  $\lambda$  4570·3 to disappear, while at the same time it brings out the green line  $b_4$  and the blue lines  $\lambda$  4481 and  $\lambda$  4703·5, which are reversed in the solar spectrum. Thus lithium, potassium, and magnesium are examples of elements which are not so completely dissociated by the flame as by the solar heat. The author throws out the suggestion that these molecular states form a basis for the law of multiple proportions:—"Then the metals in different chemical combinations will exist in

different molecular groupings, and we shall be able by spectrum observations to determine the particular heat-level with which the molecular complexity of the solid metal, induced by chemical affinity, corresponds." V. H. V.

**Note on the Reduction of Observations of the Spectra of 100 Sun-spots observed at Kensington.** By J. N. LOCKYER (*Proc. Roy. Soc.*, **32**, 203).

**Photographic Spectra of Stars.** By W. HUGGINS (*Proc. Roy. Soc.*, **30**, 20—22).—The author has made a series of photographs of various planets and stars with a special apparatus, whereby the image of the star could be brought with certainty upon any part of the slit of the spectroscope, and kept there during the photographic exposure. As the slit was provided with two shutters, the solar or other spectrum could be taken on the same plate for comparison. The stellar spectra extends from about G to O in the ultra-violet. The stars of the white class exhibit a remarkable typical spectrum, which consists of twelve well-defined lines, winged at the edges. Three of the lines agree in position with the hydrogen lines,  $H_{\lambda}$ ,  $H_{\beta}$ , and  $H_{\gamma}$ ; whilst the remaining nine form a group in which the distances between any two adjacent lines is less as the refrangibility increases; it is probable that from their intimate connection with one another, they represent one substance.

In the stars of the above-named class, the line  $H_{\delta}$  is either absent or very thin as compared with its appearance in the solar spectrum, whereas in the case of Arcturus, which belongs to the solar type, this line is broader and more intensified than in the solar spectrum. The white stars may be arranged in a series in which the line  $H_{\delta}$  passes through definite stages of thickness, whilst the typical lines become more defined; Arcturus, on the other hand, gives a spectrum on the other side of that of the sun.

The photographs of the planets show no sensible modification of the violet and ultra-violet parts, and the spectra of small areas of the moon's surface point to no absorptive action of a lunar atmosphere.

V. H. V.

**Spectrum of the Flame of Hydrogen.** By W. HUGGINS (*Proc. Roy. Soc.*, **30**, 576—580).—The author has taken the photographs of spectra of different flames containing hydrogen. The spectrum of the flame of hydrogen burning in air consists of a series of lines from  $\lambda$  3062 to  $\lambda$  3276, of which the group proper of water commences with a strong line  $\lambda$  3068, and can be traced in the photograph to  $\lambda$  3290. On introducing oxygen into the flame, leaving a small excess of hydrogen, a similar spectrum was obtained; on substituting coal-gas for hydrogen, the spectrum contained the characteristic water group, and in addition a strong line close to G, and two lines  $\lambda$  3872 and  $\lambda$  3890; but the ultra-violet group compared with the group in the spectrum of pure hydrogen showed several small differences. With a double Bunsen burner supplied with a strong blast of air, or when a spirit lamp was used, spectra were obtained similar to those of the coal-gas-oxygen flame. The distinctive features of these three last-named flames appear to be connected with the presence of carbon.

V. H. V.

**Spectrum of Water.** By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*, **30**, 580—582).—The authors have noticed, in the course of their experiments on the nitro- and hydrocarbon spectra, a remarkable series of lines in the ultra-violet part of the solar spectrum between the lines S and R. This spectrum commences at its more refrangible end with two strong bands,  $\lambda$  3062 and  $\lambda$  3068, and extends up to  $\lambda$  3210; it is attributed by the authors to water. It is well developed in the flame of hydrogen and of the hydrocarbons burning in oxygen, and less strongly in non-hydrogenous gases, if burnt in moist oxygen. An apparatus was constructed by means of which the spectra of the electric spark in dry and moist gases could be compared. Gases rendered dry by phosphoric anhydride gave only the faintest traces of the spectrum alluded to above, but on introducing a drop of water, the spectrum became well developed. When a condenser is used, the water spectrum disappears. The authors consider that these facts will modify the conclusions which have been drawn as to the characters of the specific absorption of water. V. H. V.

**Note of the History of the Carbon Spectrum.** By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*, **30**, 490—494).—A historical and controversial communication.

**Spectrum of Carbon.** By J. N. LOCKYER (*Proc. Roy. Soc.*, **30**, 335—343, and 461—463).—At the commencement of this paper the author brings forward quotations from the works of Attfield, Morren, and Watts, in order to controvert the conclusions arrived at by Liveing and Dewar with regard to the hydro- and nitro-carbon spectra. In experiments in which photographs of the electric spark were taken in carbon tetrachloride, the sets of flutings assigned by Liveing and Dewar to the hydrocarbons and cyanogen was seen simultaneously; but if the coil be connected with a Leyden jar, these flutings will vanish, and the line spectra of chlorine and carbon take their place. Further, the undoubted spectrum of cyanogen is visible neither in the electric arc, nor in the surrounding flame. These results confirm the work of Attfield and Watts, that the spectrum consisting of the flutings in question, is due to the element *carbon*. According to the author, it is probable that the sets of carbon flutings represent different molecular groupings of carbon, in addition to those which give the line spectrum, and that the various flutings are dependent upon the tension of the electric current.

The author has taken photographs of the spectra of the various carbon compounds under various conditions, in order to mark and map out the coincident lines and flutings. The phenomena seen with various degrees of constancy are a blue line,  $\lambda$  4266, a set of blue flutings,  $\lambda$  4215— $\lambda$  4151, and a set of ultra-violet flutings,  $\lambda$  3885—3843. In the spectrum of the electric arc the blue flutings alone are visible, but in the case of the spark, the ultra-violet flutings and the blue line are visible whilst the blue flutings are faint. These observations are in accordance with the hypothesis advanced by the author, that the lines presented in the spectra are dependent on the temperature of the substances producing the spectra. In this case, the blue flutings

correspond with the lowest, the blue line with the highest, and the ultra-violet flutings with the intermediate temperature. On thus comparing the spectra of carbon under various conditions, it is found that the *blue line never appears in conjunction with the blue flutings, unless the ultra-violet flutings are also present*; or the highest and lowest hypothetical temperature spectra are never visible without the spectrum of the intermediate hypothetical temperature. In the paper various diagrams of the photographed spectra of carbon are given in support of the hypothesis.

V. H. V.

**Spectra of Compounds of Carbon with Hydrogen and Nitrogen.** By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*, **30**, 152—162, and 494—509).—The authors at the outset allude to the observations of Ångström and Thalèn, and others, on the different spectra of carbon and its compounds under different conditions. The authors have made a series of observations on the spectra of the electric arc in various gases and of the flames of carbon compounds. It is shown, firstly, that the characteristic spectrum of cyanogen, viz., seven blue, violet, and ultra-violet bands, is conspicuous in the arc when taken in an atmosphere of nitrogen, air, nitric oxide or ammonia, but that these bands disappear in a non-nitrogenous atmosphere of hydrogen, carbonic oxide and anhydride or chlorine. These same bands appear in the flames of cyanogen and hydrocyanic acid, but not in those of hydrocarbons, carbonic oxide, or carbon bisulphide. Hence it appears that these particular bands belong only to cyanogen. Secondly, the characteristic green and blue bands of the hydrocarbon flames are well seen in the arc when taken in nitrogen and chlorine, but are always present whatever be the atmosphere, owing to the presence of hydrogen in the carbon electrodes. These bands appear also in the flames of the hydrocarbons and their derivatives, but are not seen in the flames of other carbon compounds, even when mixed with hydrogen. These facts confirm the observations of Ångström and Thalèn, that these green and blue bands are characteristic of acetylene. Attention is also drawn to the similarity of the magnesium hydrogen spectrum with that of the hydrocarbons, which points to the probability of a compound of magnesium and hydrogen analogous in constitution to acetylene. The authors consider that the variations of the length and character of the electric discharge in different gases, is, among other factors, dependent upon the relative facility with which the carbon electrode combines with a gaseous medium.

In order to prove that the seven blue, violet, and ultra-violet rays, referred to above are due to cyanogen only, an examination has been made of the spectrum of the electric spark in carbon tetrachloride. The photograph shows no trace of these lines, provided that all the air has been exhausted from the globe containing the vapour of the tetrachloride; but on introducing even  $\frac{1}{600}$  part of its volume of nitrogen these bands immediately made their appearance. Similar results were obtained with carbon bisulphide, benzene, and naphthalene. With carbonic oxide no nitrocarbon bands could be observed, but they become visible on introducing a small bubble of air. The



authors consider that Watts' observation of these nitro-carbon bands in the spectrum of the arc in naphthalene and carbonic oxide was due to the presence of nitrogen impurities. Experiments are also quoted to illustrate the sensibility of this spectroscopic test for nitro-carbon compounds. As in all the experiments, the bands assigned by Ångström and Thalèn to the hydrocarbons were plainly visible, it is evident that much more care than has generally been thought necessary is requisite to remove the last traces of hydrogen and its compounds from spectral tubes; even phosphoric anhydride is inadequate to remove the last traces of water. In conclusion, the authors meet the criticisms of Lockyer on their results.

V. H. V.

**Spectrum of Carbonic Anhydride.** By C. WESENDONCK (*Proc. Roy. Soc.*, **32**, 380—382).—The spectrum first observed by Swan at the inner cones of flames of burning liquid and gaseous carbon compounds has been ascribed by Atfield and Watts to the element carbon, but by Thalèn, Ångström, and Liveing and Dewar (preceding Abstract), to a combination of hydrogen with carbon. As the latter attribute the appearance of Swan's spectrum, when an electric discharge is passed through a Geissler tube filled with either of the oxides of carbon, to the presence of traces of moisture, the author has made a series of experiments with carbonic anhydride dried with the utmost care. The apparatus used was exhausted, until on the passage of the current the green hydrogen line was invisible, and carbonic anhydride introduced, which had been in contact for 12 hours with phosphoric anhydride; on the passage of the electric current, Swan's spectrum was visible, and that, even at low pressures, when a Leyden jar was used. These experiments prove that Swan's spectrum cannot be ascribed solely to a combination of carbon with hydrogen. Slightly different results were obtained, when the distance of the electrodes was shortened; Swan's spectrum was invisible, although the carbonic anhydride had not been dried with the utmost care. The author makes some remarks on the correlation between the different orders and forms of the spectra and the conditions of the electric discharges.

V. H. V.

**Identity of Spectral Lines of Different Elements.** By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*, **32**, 225—231).—The authors allude to the interest attached to the question of the identity of the spectral lines, and to the improbability of single homogeneous molecules taking up the variety of vibrations indicated by the complex spectrum of iron or titanium. Inasmuch as Lockyer has made this supposed identity the basis of a theory of the dissociation of the elements into simpler constituents, the authors have examined the question by confronting the bright line spectra of the various metals under a powerful dispersion, the source of light being the electric arc taken in a crucible of magnesia or lime. In order to resolve the supposed coincidences, one metal was introduced into the crucible, and the line to be observed placed at the pointer of the eye-piece; the second metal was then introduced, and in most cases *two* lines were seen where only one was visible before. The authors have thus resolved most of the supposed identical lines of iron with those of

titanium, calcium, nickel, manganese, magnesium, chromium, and cobalt, and of calcium with those of chromium, cobalt, nickel, barium, and cadmium.

Inasmuch as from these experiments hardly a single coincidence can be established, even in the complex spectra of iron and titanium, it is most probable that the materials of these metals, even if they be not homogeneous, are still different from those of other chemical elements. The resolution of different elements into simpler constituents thus receives no support from the most powerful method of analytical investigation.

V. H. V.

**Reversal of the Lines of Metallic Vapours.** By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*, **32**, 402—405).—Attention is drawn at the outset to the difficulty of obtaining a reversion of the lines of the iron, titanium, and chromium spectra, although many of these lines are represented among the Fraunhofer lines. When iron is put in a crucible through which the arc of a Siemens dynamo-electric machine is passing, and fragments of magnesium dropped in, the authors have observed the reversal of the iron lines about the solar lines L and N, four strong lines below N, the line O, all the strong lines from S<sub>2</sub> to U, and two strong groups still more refrangible. By introducing a stout iron wire into the axis of the positive carbon, and passing a gentle stream of hydrogen gas through the negative carbon, the strongest lines of iron are reversed, and the weaker lines are seen to expand and then are reversed. By this means the authors have succeeded in reversing 137 of the iron lines, including, besides those mentioned above, the lines E, b<sub>4</sub>, G, s; it is however found that it is not always the strong lines which are reversed. On the whole, the phenomena in the case of iron are of much the same general character as those observed in the case of the other metals.

When the perforation of the positive carbon is filled with titanium cyanide, the titanium lines, especially in the green and blue parts of the spectrum, are expanded and reversed.

In the case of chromium, on the passage of a current of hydrogen or coal-gas, the following lines and groupings were reversed; the triplet in the green, three strong lines in the indigo, a triplet near N, a strong double line below O, and the triplet,  $\lambda$  2799.8,  $\lambda$  2797,  $\lambda$  2794, and a line  $\lambda$  2779.6. The two aluminium lines near  $\delta$  are frequently reversed when a fragment of the metal is dropped into the crucible.

V. H. V.

**Spectrum of Magnesium and Lithium.** By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*, **30**, 93—99).—In this paper, attention is drawn to spectra of magnesium and lithium under various conditions, with more especial reference to the green line  $\lambda$  5210. The spark spectrum between magnesium points in perfectly dry nitrogen and carbonic oxide gave no indications of the line 5210, but on introduction of traces of hydrogen or moisture, the line made its appearance. The spark in hydrogen at atmospheric pressure gave indications of the line; but on reducing the pressure below 180 mm., the line disappeared; similarly the line was not visible in the arc in a lime or carbon crucible, but it appeared on the passage of a stream of hydrogen

through the electrodes. This line, as well as an attendant series of fine lines, appears in the flame of magnesium burning in air; but they are more brilliant if the burning magnesium is introduced into a jet of hydrogen or coal-gas. The authors ascribe this line  $\lambda$  3210 and its attendant series to a mixture of magnesium and hydrogen; for it is shown by independent evidence that mixtures favour the production of certain vibrations, which are not so strong or not visible with the elements of those mixtures taken separately. The spectrum of magnesium in the arc consists of lines at 5510.7, 5527.5; the *b* group, 4703.5, 4570.5, 4351.2, 4166, 4057.3, and the triplet beyond H. In the spectrum of lithium, besides the line  $\lambda$  4131.7 (Boisbaudran), the authors have observed a line 4273, and two more lines on either side of H and K of wave-lengths 3913 and 3984. V. H. V.

**Spectrum of Magnesium.** By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*, **32**, 189—203).—The authors have carried out a series of investigations on the spectrum of magnesium in order to bring out the connection between its variations under different conditions, and to study the question of the emissive power for radiations for short wave-lengths at relatively low temperatures. In the spectra of the flame of burning magnesium of the arc fitted with a lime crucible, and of the spark of an induction coil between magnesium points, appear the three lines of the *b* group, the blue line  $\lambda$  4570, the triplet in the ultra-violet between K and L, and the line  $\lambda$  2850: the last is the most persistent and strongest, and is easily reversed; and is remarkable for its power of expansion. The series of triplets are equally characteristic, the least refrangible pair appearing in the flame spectrum, others in the spark, but the complete series in the arc. The authors regard these triplets as a series of harmonics, but do not consider that the appearance of the complete series in the arc is due solely to the elevated temperature. The blue line  $\lambda$  4570 of the flame is seen in the arc, but in the spark it crosses the field in occasional flashes. The series of bands near L, which are only characteristic of the flame spectrum, appear to be the spectrum of a compound, but the authors have been unable to trace them to any particular combination; the triplet at M, with which these bands end, resembles in its general character the other magnesium triplets, but its presence in the flame spectrum alone is not easily explained. Attention is also drawn to the presence of the triplet in the ultra-violet and the line  $\lambda$  2850 in the flame spectrum, as corroborating the results obtained in the examination of the ultra-violet spectrum of water; that in the regions of shorter wave-lengths substances at the temperature of flames give discontinuous spectra, which have hitherto been considered to be characteristic of the highest temperature. In the arc and spark spectra, but not in that of the flame, there appears a group of two strong lines,  $\lambda$  2801 and 2794, and a quintuple group; there are besides several single lines, which may be developed by the temperature of arc and spark. A pair of lines in the arc spectrum near U appears slightly shifted in the spark spectrum; this shifting is, however, probably not due to a selective action by which the electric discharge lights up certain kinds of matter in its path to the exclusion of others.

The spark spectrum of magnesium varies with the pressure of the medium in which the electrodes are enclosed; certain of the blue and yellow lines were enfeebled, and finally disappear. In this respect the magnesium spectrum resembles that of nitrogen observed by Cazin.

The authors show that certain lines observed by Fievez in the dark spectrum of magnesium were the so-called *ghosts*, which are images of brighter lines caused by the Rutherford gratings. A description is also given of the magnesium hydrogen spectrum, which is assigned by the authors (p. 255) to a mixture of hydrogen and magnesium. It consists of a series of flutings beginning with lines of wave-lengths  $\lambda$  5618, 5566, and 5513, 5210, 4849, and 4803, of which the set in the green 5210 is the most marked. It is shown that the brilliancy of this magnesium hydrogen spectrum increases when the pressure of the hydrogen in which the magnesium electrodes are enclosed is increased, which points to the supposition that this magnesium hydrogen combination resembles the hydrides of palladium and sodium, in that increased pressure renders the compound more stable, as shown by the greater brilliancy and continuity of the spectrum. In conclusion, after all simplifications by eliminating the magnesium-hydrogen flutings, and supposing the whole series of triplets to be harmonically related, the fact remains that the chemical atoms of magnesium are either capable of taking up a great variety of vibrations by themselves, or by their mutual action on each other, or on particles of matter of other kinds. Extended series of observations will be required in order to trace the correlation of the various vibrations and the conditions on which they are dependent.

V. H. V.

**Luminosity of the Flame of a Bunsen Burner induced by Heating the Tube.** By R. BLOCHMANN (*Annalen*, 207, 167—193).—The fact that the flame of a Bunsen burner is rendered luminous by heating the tube in which a platinum tube is placed, is classed by Wibel in the same category as the phenomena of revived luminosity in the case of gas-flames rendered non-luminous by the admixture of some inert gas such as nitrogen, steam, &c. The revived luminosity can, however, in the latter cases be traced directly to the rise in temperature; whereas in the Bunsen flame it may be due to various other causes. Among the first of these may be mentioned the question as to whether the relative proportion of air and gas in the flame is altered by heating the tube. Experiments in this direction showed that while the proportion of gas to air in the flame of a burner under ordinary conditions was 1 to 1.58, when the tube was heated to redness this proportion was changed to 1 to 0.43, only about one-third of the original amount of air being admitted; that the strength of the current of air drawn into the holes was lowered on heating the tube was also conclusively shown by placing pieces of thin aluminium foil near the apertures. When the tube was heated, they had to be moved nearer to the apertures in order to be drawn in. A mixture of 38.7 volumes of gas and 61.3 volumes of air was passed through a red-hot platinum tube: on collecting and analysing the gas issuing from the tube, it was found that combustion had taken place, and that the oxygen had completely disappeared; the hydrogen had been almost completely

burnt, only a small proportion of the hydrocarbons having been attacked; the character of the gaseous mixture had therefore been completely changed. This partial combustion also takes place in a heated glass tube, but in this case tarry products are also formed. Such a mixture of gases cannot therefore be compared with the gases in an ordinary Bunsen flame; it has a closer resemblance to a non-luminous mixture of coal-gas with nitrogen or carbonic anhydride, and conclusions cannot be drawn from the behaviour of such a mixture with reference to the cause of the non-luminosity of a Bunsen flame.

Heumann explains the renewed luminosity when the tube is heated to the rise in temperature, whether the flame has been made non-luminous by air or by an inactive gas; and the flame of a Bunsen burner being considerably hotter than that of coal-gas mixed with nitrogen or any other inactive gas, he assumes that the same relative difference of temperature holds good when the tube is heated to redness. That this is not the case is shown by the fact that a piece of silver which readily melted in the ordinary Bunsen flame began to melt after some time only, when the tube of the burner was heated. According to Landolt's figures, the chief difference between a luminous and non-luminous Bunsen flame is, that the former has more nitrogen and less combustible material in its interior than the latter; the reason of the non-luminosity can therefore lie only in the presence of oxygen in the latter. Air strikes the luminous flame from all directions, and the combustion begins where the air meets the flame, and continues into the interior as far as the oxygen of the air suffices. This region of combustion appears as a thin blue stratum covering the flame, and the heat evolved therein acts on the unburnt and included gas, causing it to decompose and separate carbon, by the incandescence of which the flame becomes luminous. To ensure luminosity, therefore, such hydrocarbons must be present as will yield carbon on decomposition, and the heat generated in the region of combustion must be sufficiently great to cause this decomposition. It is therefore easy to understand why coal-gas mixed with nitrogen, carbonic anhydride, or steam, burns with a non-luminous flame; for apart from the diluting action of these gases, they absorb a great part of the heat, and the remainder is not sufficient to decompose the hydrocarbons. When, however, the mixture of gases is heated before ignition, the heat is raised sufficiently to counteract the diluent and absorbent effects of the inert gases, and a luminous flame is the result.

In the flame of a Bunsen burner the case is altered. Here the gas is already mixed before ignition with one-third of the oxygen necessary for its combustion, and on reaching a proper temperature begins to burn in the centre of the flame; here the heavy hydrocarbons completely disappear, only six per cent. of combustible material passing unchanged into the outer region of the flame. When the mixture of air and coal-gas is heated to redness before ignition, the issuing gas has no longer the same composition, but may be compared to a coal-gas robbed of most of its hydrogen and diluted with nitrogen and steam. Such a mixture when heated would of course give a luminous flame, provided that the quantity of the diluents was not too large; it is in fact still luminous when the mixture is first allowed to

cool. All therefore that Wibel's experiment virtually tells us is, that a flame partially deluminised with nitrogen and steam becomes again brightly luminous on heating the issuing mixture of gases.

J. K. C.

**Chloride of Silver Battery.** By W. DE LA RUE and H. MÜLLER (*Proc. Roy. Soc.*, 30, 563—572).—The authors have employed the silver chloride battery to examine the question whether there is a polarisation of the terminal of a vacuum tube after the discharge through it has been interrupted by breaking connection between it and the source of electricity: if so, is this polarisation similar to the chemical polarisation of the terminals of a voltameter? By a series of experiments, it was proved that the current obtained from the terminals of a vacuum tube, after having been disconnected from the battery, is solely due to a static charge and not to a chemical polarisation.

V. H. V.

**A Voltaic Cell.** By J. B. OSTER (*Chem. Centr.*, 1881, 721).—The author has constructed a powerful and permanent voltaic cell by covering sheet lead with a sufficiently thick coating of lead peroxide; the sheet is then wrapped in flannel, an anode of copper soldered on, and the whole rolled tightly in a cylinder. It is then enclosed in a wrapper of sheet lead, and introduced into a clay cell filled with dilute sulphuric acid; the cell is placed in a glass vessel filled with acid of the same strength, and containing amalgamated zinc plates. This cell gave a deviation of 70° of the galvanometer for four days. The author proposes to modify this element with a view of constructing a Faure's accumulator, and has given notice of the patent.

V. H. V.

**New Electrical Storage Battery.** By H. SUTTON (*Chem. News*, 44, 298—299).—The principle of this battery consists in retaining the hydrogen which is liberated when the battery itself is charged. For this purpose the positive electrodes consist of lead plates amalgamated with mercury (whereby polarisation effects, and local action are reduced to a minimum) and the negative electrodes of copper, the solution between the electrodes being copper sulphate. The plates are perforated with a number of holes and rolled into a spiral, being separated from one another by rubber bands, cut every 5 inches to allow of the perfect circulation of the solution. This combination is immersed in the copper sulphate, and the amalgamated lead plates made the positive pole of an electric battery. The lead uniting with the oxygen becomes uniformly coated with peroxide, and the liberated hydrogen decomposes the copper sulphate, forming sulphuric acid, and the copper is deposited on the copper plate. As the action continues, the colour of the copper sulphate gradually disappears, and when it is complete, the solution becomes colourless, and contains sulphuric acid. The battery is now ready for use, and during its discharge the peroxide is reduced, and the copper oxidised and dissolved by the acid, forming again copper sulphate. This form of battery is very constant and powerful, the decomposition and re-formation of one pint (?) of copper sulphate doing sufficient work to heat to a red heat 1 inch of No. 28 iron wire for two hours.

A practical form of cell may be made by fixing a series of lead plates in a box in grooves, filling between the plates with a solution of copper sulphate, and passing through the cell a current of sufficient tension to overcome the contrary electromotive force of the series, the positive sides of the plates being peroxidised, and the copper being deposited on the negative. Batteries of great tension can thus be charged from 30 Bunsens.

In place of copper and copper sulphate, zinc and zinc sulphate, or iron and iron sulphate may be used for the negative electrode solution. The zinc, however, requires amalgamation to prevent local action, and the iron oxidises when the cell is not in use, therefore these forms are objectionable.

L. T. O'S.

**Studies on the Electric Arc.** By J. DEWAR (*Proc. Roy. Soc.*, **30**, 85—93).—The author has examined the influence of impurities in the carbons on the production of cyanogen compounds in the electric arc. Carbon poles heated continuously for several days in a rapid stream of chlorine to volatilise the silicon, aluminium, and iron as chlorides, still yielded hydrocyanic acid when a current of air was drawn through the positive pole. The electric arc, when enclosed in an atmosphere rendered as free from moisture as possible, produced considerable quantities of hydrocyanic acid. Similar results were obtained with carbon tubes enclosed in a block of limestone; but when dry hydrogen was passed through the positive pole, only a trace of hydrocyanic acid was formed, and pure dry air gave no traces of hydrocyanic acid or acetylene. Determinations are also adduced of the amount of nitrites produced in the arc of a Siemens lamp and of Jablochhoff's candles with De Meritens' highest intensity current; the mean of several experiments with the former was 509 mgrms., with the latter 930 mgrms. per hour. By a series of experiments, the author proves that the intensity of the total radiation of the positive pole of the Siemens arc is ten times that of the same substance at the temperature of the oxy-hydrogen blowpipe flame; and that it may be inferred that the temperature of the former is about 6000° C., if that of the latter be taken as 2000°.

V. H. V.

**Action of Cold on the Voltaic Arc.** By D. TOMMASI (*Compt. rend.*, **93**, 716—717).—If the voltaic arc plays between two copper U-tubes (through which a rapid current of cold water is running), placed horizontally opposite one another, we observe that—1. The luminosity of the arc is greatly weakened, a current from 75 large Bunsen elements giving only a luminous point. 2. The arc is very unsteady, the slightest draught extinguishing it. 3. That a piece of paper placed 4 or 5 mm. above the arc chars but does not take fire. 4. The arc is simply a luminous globule, moving up and down between the two tubes, resembling a drop of liquid in the spheroidal state. 5. If a magnet is presented to the arc, it is attracted by the magnet, leaves the U-tubes, and is consequently extinguished. 6. Apparently there is more ozone produced than when the arc is not cooled. The arc is coloured slightly green, showing that a part of the copper burns in spite of the cooling.

D. A. L.

**Effects of Electric Currents on the Surfaces of Mutual Contact of Aqueous Solutions.** By G. GORE (*Proc. Roy. Soc.*, **30**, 322—323).—The author has made a series of experiments to ascertain whether an electric current passing between two aqueous liquids affects their diffusion into each other. It was found that, when a current was passed between the surfaces of mutual contact of certain aqueous solutions of different specific gravities, the line of demarcation became ill-defined when the current passed from the lighter to the heavier solution. On reversing the direction of the current, the line of demarcation again became well defined. These observations were confirmed by repeatedly reversing the direction of the current after suitable intervals of time, when the effects were reversed with each such change.

V. H. V.

**Refraction of Electricity.** By A. TRIBE (*Proc. Roy. Soc.*, **32**, 435—443).—In order to examine whether electricity, like other forms of energy, is endued with the property of refraction, the author has traced out the alterations of direction of energy when electricity passes from one electrolytic medium to another of different conductivity. Two sheets of gutta-percha were fixed across an electrolytic cell of copper sulphate, inclined at an angle of  $45^\circ$  to the base line; into the inner cell enclosed by the gutta-percha walls a 1 per cent. copper sulphate solution was introduced, and in the outer cells a concentrated solution of the same salt. The distribution of energy was recorded by the immersion in both cells of rectangular silver plates, called *analysers*, placed lengthwise in several parts of the central line joining the electrodes. A unit current was employed, and copper electrodes of the breadth and depth of the outer cells. By the aid of this apparatus and suitable modifications of the experiments, the author shows (1) that electricity, in passing obliquely from one medium to another, is refracted towards the perpendicular when from a better to a worse conductor, but from the perpendicular when from a worse to a better conductor; (2) the refraction increases or decreases according to the relative conductivity of the two media; (3) the refraction increases as the angle of incidence increases, it being probable that the sines of the angles of incidence and refraction are in constant ratio.

In an added note, Professor Stokes points out that according to theory, the tangents, not sines, of the angles of incidence and refraction are in constant ratio, but owing to the introduction of errors the numbers adduced cannot be deemed sufficient to decide between the laws of sines and tangents. Further, in the case of the second medium being the better conductor, the law of sines would lead to extravagant results.

V. H. V.

**Limits of Electrolysis.** By BERTHELOT (*Compt. rend.*, **93**, 661—668).—The electromotive force necessary to produce electrolysis can be calculated in three different ways. With potassium sulphate, for example, there is: 1st. The separation of the sulphuric acid, oxygen, and potassium, which would require 98 calories. 2nd. Supposing the necessary electromotive force differs but slightly from that required to decompose dilute sulphuric acid, it would then equal 34.5 cal.



3rd. But if in addition to the 2nd, the separation of the acid and the base be taken into account, then a force equal to 50·2 cal. would be required. The author shows that the 3rd is the right supposition, by the electrolysis of potassium sulphate with platinum electrodes. Moreover, by employing mercury for the negative electrode, he finds that in order to obtain potassium amalgam, at least 4 D. (98 cal.) were necessary. Although the electrolysis of the potassium sulphate without the formation of amalgam takes place with 2 D. + Zn—Pt (68 cal.), this is accounted for when we take into account the heat of formation of the liquid amalgam, 25·7 cal., then  $68 + 25·7 = 93·7$ , or nearly the theoretical (98). The decomposition of acidulated water by a single couple, zinc and sulphuric acid (Tommasi, *Compt. rend.*, **93**, 638), can be thus explained:—For if the positive electrode is a metal capable of uniting with oxygen, copper for instance, then while the hydrogen is given off at the negative pole, the copper is oxidised and forms sulphate, giving out 28·2 cal.; the acidulated water would then only require an excess electromotive force  $= 34·5 - 28·2 = 6·3$  cal.; this is much less than that given by the zinc in dissolving (19 cal.) Other sulphates, such as magnesium sulphate, behave in a manner similar to potassium sulphate. The electromotive force required for the decomposition of zinc sulphate is equal to that necessary for the separation of the base and the acid, plus that required for the decomposition of the former into the metal and oxygen. If, however, copper be used for a positive electrode, the zinc can be precipitated with 1 D.; this is accounted for by the fact that the copper sulphate solution formed is not of the same concentration as the zinc sulphate solution. With potassium chloride, gas is given off, with  $2\text{Zn} - \text{Pt} + 1\text{Cd} - \text{Zn}$  (46 cal.), which shows that the electrolysis of potassium chloride does not necessarily require the setting free of the metal, but that it really is equivalent to the formation of potassium hydroxide and hydrochloric acid (13·7 cal.), plus the decomposition of the latter (33 cal.). The electromotive force necessary to decompose potassium bromide is equal to 40 cal., which corresponds with the decomposition into potassium and bromine (91 cal.), minus the 47·5 cal. due to the generation of potassium hydroxide, and 2 cal. from the formation of a perbromide. Fluoride of potassium requires 50 cal., which is equal to the separation of the base and acid (16·5 cal.) plus the liberation of the hydrogen and oxygen of the water (34·5 cal.). Potassium iodide was decomposed with Zn—Pt + Zn—Cd (27 cal.) with separation of hydrogen and iodine. The number 27 is equal to the separation of potassium and iodine, less the formation of potassium hydroxide, and represents the sum of the decomposition of the salt into potassium hydroxide and hydriodic acid (13·7 cal.), and of the latter acid into iodine and hydrogen (13·2).

It will hence be seen that the haloïd salts behave in a manner analogous to potassium sulphate; and that in both cases the minimum energy necessary to produce decomposition is very much less than that required to set free the alkali-metal.

D. A. L.

**Chemico-electric Relations of Metals in Solutions of Potassium Salts.** By G. GORE (*Proc. Roy. Soc.*, **30**, 38—48).—The author

has made a series of experiments on the chemico-electric positions of various metals in solutions of salts of potassium of various strengths and at different temperatures; the results are recorded in a series of tables. Note is also taken of the temporary reversals of the current, other than those which take place immediately on immersion. The author finds: (i) that the greater number of temporary reversals occur in potassium cyanide solution; (ii) that the proportions of such reversals to the number of solutions employed was not greatly different in potassium chloride, bromide, or iodide; and (iii) these reversals were not confined to the more electro-positive metals.

The following general results are also arrived at: (i) gas carbon is electro-negative to all other bodies in the solutions employed; (ii) rhodium or platinum is electro-negative to all bodies except carbon; (iii) magnesium is positive to all other substances in potassium chloride, bromide, or iodide; and (iv) magnesium, aluminium, or zinc is positive to all other metals in solutions of potassium cyanide. It was found that the positions of pairs of metals of similar properties, such as magnesium and zinc, nickel and cobalt, &c., often varied together and described similar curves or lines of variation.

V. H. V.

**Electrical Properties of Indium.** By T. ERHARD (*Ann. Phys. Chem.* [2], **14**, 504—508).—1. *Resistance*.—In the following table, the first column gives the temperature at which the determination was made, the second the resistance of the indium wire in mercury units; the third the specific resistance as actually found; the fourth the specific resistance calculated from the formula  $S = a + bt + ct_2$ ; and the fifth column the differences between the found and calculated values of S:—

<i>t.</i>	<i>r.</i>	S.		Diff.
		Found.	Calc.	
— 5·4° C.	0·3019 S.U.	0·0870	0·0868	— 0·0002
— 5·2	0·3024	0·0871	0·0868	— 0·0003
+ 16·5	0·3341	0·0962	0·0960	— 0·0002
17·7	0·3345	0·0964	0·0965	+ 0·0001
18·5	0·3364	0·0969	0·0968	— 0·0001
25·7	0·3474	0·1001	0·0999	— 0·0002
38·6	0·3654	0·1053	0·1053	0
58·4	0·3934	0·1133	0·1137	+ 0·0004
80·0	0·4274	0·1231	0·1228	— 0·0003
96·0	0·4509	0·1299	0·1296	— 0·0003

2. *The thermo-electric position of indium*, compared with the following eight metals, for a temperature difference between 0° and 98·6°, is shown by the series—

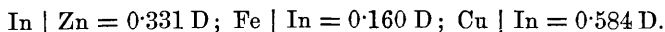
— Al, Sn, In, Zn, Ag, Au, Cu, Fe +

and for a small temperature difference (0—5°) or (0—10°) by the series—

— Al, Sn, Au, Zn, In, Ag, Cu, Fe +

3. *Position in Electromotive Series*.—In the element In | Zn, the in-

dium is positive, whilst in the elements  $\text{In} \mid \text{Fe}$  and  $\text{In} \mid \text{Cu}$  it is negative; the electromotive powers for the several elements being as follows:—



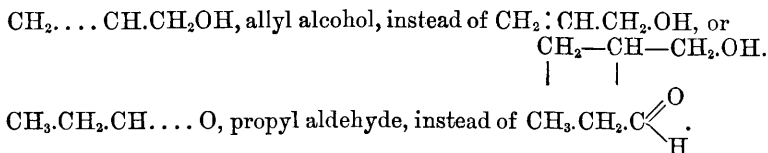
T. C.

**Relation between the Optical and Thermal Properties of Liquid Carbon Compounds.** By J. W. BRÜHL (*Monatsh. Chem.*, 1881, 716—774).—Not only the heat evolved by the combustion of 1 gram of an organic compound, but also the specific refraction of the substance is diminished, either by the union of the compound with one or more atoms of oxygen, by loss of hydrogen, or by the displacement of hydrogen by oxygen. For example, the specific refraction and heat of combustion (for equal weights) of an acid is lower than that of the corresponding aldehyde, and the values for the aldehydes are lower than those for the corresponding alcohols. In homologous series, the decrease in specific refraction or heat of combustion produced by the elimination of 2 atoms of hydrogen, or by the displacement of hydrogen by oxygen, diminishes with the increasing molecular weight of the compounds.

The sp. gr. increases, but the specific refraction and heat of combustion (for equal weights) decrease when hydrogen is displaced by chlorine. The specific refraction and heat of combustion of equal weights of chlorides are higher than for the corresponding bromides, and for bromides than iodides. In homologous series, these values also increase with the molecular weight, but the difference produced by the increment,  $\text{CH}_2$ , diminishes as the molecular weights increase.

Isomeric compounds in which the atoms have the same degree of saturation, have the same specific refraction, and also evolve the same amount of heat on combustion. Polymerisation lowers both these values.

Compounds containing carbon-atoms which are supposed to be united by so-called double linking, have a higher specific refraction and a higher heat of combustion than their isomerides in which double linking does not occur. From this fact, the author concludes that the compounds in which double linking is supposed to exist, really possess free affinities. The oxygen or carbon atoms, which are usually believed to be united by double linking, are only feebly attached to each other: hence it is proposed that the ordinary formulæ for these compounds should be discarded and others substituted, *e.g.*:—



The benzene nucleus would be represented thus:—



W. C. W.

**Nitric Oxide as a Supporter of Combustion.** By BERTHELOT (*Compt. rend.*, **93**, 668—674).—Nitric oxide contains more than 50 per cent. of oxygen, and this oxygen in combustion disengages 21,600 cal. more than free oxygen; nitric oxide ought, therefore, to be a more active supporter of combustion than the latter; this, however, as is well known, is only the case under certain circumstances; but, until now, nobody has offered an explanation of this anomaly.

Mixtures of nitric oxide, hydrogen, and oxygen, in proportions  $\text{NO} + \text{H}_2 + \text{O}_2$  and  $\text{NO} + \text{H}_2 + 2\text{O}_2$ , give rise to the production of nitric peroxide alone without formation of water. Moreover, a mixture of hydrogen and nitric oxide is not fired by the electric spark or a body in combustion, for the heat is only sufficient to decompose the nitric oxide into nitrogen and oxygen, the latter combining with the undecomposed nitric oxide.

The reaction between hydrogen and nitric oxide can, however, be effected by means of a series of sparks. A mixture of  $\text{NO} + \text{H}_2$  was reduced to half its bulk under these circumstances, and at the end of some hours the nitric oxide had disappeared, but there was still free hydrogen, some of the oxygen having been used up to form basic nitrates with the mercury over which the experiments were conducted. The oxidation of the hydrogen takes place in three stages:—

- (1.)  $2\text{NO} = \text{N}_2 + \text{O}_2$
- (2.)  $2\text{NO} + \text{O}_2 = \text{N}_2\text{O}_4$
- (3.)  $\text{N}_2\text{O}_4 + 4\text{H}_2 = 4\text{H}_2\text{O} + \text{N}_2$ ,

the formation of nitric peroxide being intermediate. Hence it is necessary to decompose not nitric oxide but nitric peroxide, which requires an excessively high temperature; this is a further explanation why a flame or spark is not hot enough. A mixture of carbonic oxide and nitric oxide behaves in a similar manner, the temperature produced not being sufficient to burn all the carbonic oxide and convert it into carbonic anhydride, and, therefore, nitric peroxide and basic mercury nitrate are formed. The reason why the carbonic oxide from fulminate of mercury (*Compt. rend.*, **93**, 617) burns so suddenly in the atmosphere of nitric oxide, is because the oxygen of the nitric oxide is set free all at once by the fulminate without passing through the stage of peroxide. Some substances burn easily in nitric oxide, and mixtures with ethylene, acetylene, and cyanogen are easily fired by spark or flame. The principal cause of this difference of combustibility is the difference of the temperatures developed by the body burning at the expense of the nitric oxide.

The comparison between ethylene and methyl ether is especially decisive with regard to this theory of the difference of temperature developed, because in each case the relation of the volume of the combustible gas to the volume of the supporter of combustion is the same, and the heat given out is nearly the same (451.1 and 443.8); but the methyl ether contains the elements of water, which lowers the temperature of combustion.

The author places the limit of temperature theoretically requisite for the production of an inflammable mixture at  $7000^\circ$ ; this high figure is probably due to the formation of the nitric peroxide from

the nitric oxide, and consequent necessity of regenerating the requisite oxygen for combustion from the former.

Nitric peroxide, however, can be destroyed by chemical means at a much lower temperature; for instance, a mixture of  $3\text{NO} + 2\text{NH}_3$  is inflammable, and the theoretical heat of combustion is only  $5200^\circ$ . But then the reaction between these gases takes place in the cold, and when oxygen is also added, it goes very easily, forming nitrogen and ammonium nitrite, which salt, at a higher temperature, is decomposed into nitrogen and water; the action really is  $2\text{NO} + \text{O} + 2\text{NH}_3 = 2\text{N}_2 + 3\text{H}_2\text{O}$ , producing 98,000 cal. Each particle of nitric oxide destroyed by the spark with formation of free oxygen, gives rise to a new reaction, giving out heat and causing the easy combustion of the mixture, when the gas employed exerts a special reaction with nitric peroxide.

D. A. L.

### Comparison of the Results of Calorimetric Measurements.

By C. v. THAN (*Ann. Phys. Chem.* [2], 14, 393—426).—The author has by this research substantially settled the basis of calorimetric measurements. These measurements have been very rarely referred directly to the theoretical heat-unit (*i.e.*, the amount of heat required to raise the unit weight of water from  $0^\circ$  to  $1^\circ$ ), but generally to the specific heat of water between  $6^\circ$  and  $25^\circ$ , or to the latent heat of water, whilst the data necessary for reduction to the theoretical unit have not been known with exactitude. The author has therefore determined with great care the specific heat of chemically pure cast silver between  $0^\circ$  and  $100^\circ$  by means of the ice calorimeter.

Regnault had already determined this constant, but referred to the specific heat of water at  $15^\circ$ . It is now possible therefore to calculate the relation of the latter unit, which has been most frequently used in determinations with the water calorimeter, to that obtained with the ice calorimeter. The author finds that 15.28725 mgrms. of mercury is the value of the ordinary heat-unit in terms of mercury. This number was verified by the determination of the specific heat of lead and of water between  $0^\circ$  and  $100^\circ$  by means of the ice calorimeter, which had previously been determined exactly by Regnault.

It is now possible to reduce the various calorimetric measurements to the ordinary, if not to the theoretical heat-unit. The author obtained the following numbers by applying this reduction to the results obtained by different observers for the heat of combustion of water, the specific heat of water at  $15^\circ \text{C.}$  being taken as the unit:—

Andrews, 1848.....	= 33,880	} At constant volume.
v. Than, 1881.....	= 33,822	
J. Thomsen, 1873.....	= 34,218	} At constant pressure.
Favre and Silbermann, 1852	= 34,426	
Schuller and Wartha, 1877	= 34,471	

The more recent results of Berthelot are not described in sufficient detail to make the reduction possible in their case. The difference between the heat of combustion at constant pressure and at constant volume amounts therefore to 408 units. The heat of combustion for

constant volume calculated from Thomsen's value amounts to 33,810 units, which agrees very nearly with that obtained directly by v. Than, and also with the older determinations of Andrews. Favre and Silbermann's, and Schuller and Wartha's numbers are, however, somewhat higher. This difference appears to be due to an erroneous arrangement of the experiments, and the author has therefore endeavoured to apply a correction. T. C.

**Physical Constants of Liquid Hydrochloric Acid.** By G. ANSDELL (*Proc. Roy. Soc.*, 30, 117—122).—The author has made a series of observations of the physical constants of hydrochloric acid liquefied in a Cailletet's apparatus. For various temperatures and pressures, determinations were made of the ratio of the volume of saturated vapour to that of the condensed liquid, the former being ascertained by observing when the air manometer ceased to show an increase of pressure on compressing the gas. It was found that the volumes of the saturated vapour and liquid gradually approach one another as the temperature nears the critical point  $51.25^{\circ}$ , and it is probable that they would become identical if the experiments could be carried up to that point. The ratio between these two volumes decreases very regularly with increase of temperature until within about two or three degrees of the critical point, when it rapidly approaches unity. Determinations were also made of the density and coefficient of expansion of liquid hydrochloric acid at different temperatures.

Temperature.	Density.	Coefficient of expansion.
$0^{\circ}\text{C.}$	0.908	—
15.85	0.835	0.00062
22.7	0.808	0.000635
33.0	0.748	0.00096
41.6	0.678	0.00123
47.8	0.619	0.00166

Liquid hydrochloric acid at  $0^{\circ}\text{C.}$  has thus not quite so high a density as liquid carbonic anhydride, and is about twice as high as that of liquid acetylene; it is rather more compressible at the same temperature than acetylene. V. H. V.

**A Fourth State of Matter.** By W. CROOKES (*Proc. Roy. Soc.*, 30, 469—472).—The author at the outset compares and contrasts the distinctive characteristics of the three states of matter, solid, liquid, and gas. If the imagination be transferred from the collection of molecules involved in these three states to an isolated molecule in space, it is found to be an inconceivable entity, possessing neither the properties of a solid, nor of a liquid, nor of a gas; so that such an individual molecule must be classed in a distinct category. Similar reasoning may be applied to a collection of contiguous molecules, whose motion is so arrested or controlled that no collisions occur; and supposing such a molecular aggregation was bodily transferred from one part of space to another, this movement would not cause the aggregation

to assume the properties of gas. These conditions constitute the fourth state of matter, which is the ultimate result of gas expansion; for by great rarefaction, the free path of the molecule is made so long that the collisions with other molecules in a given time may be disregarded in comparison with the misses, in which case the molecule obeys its own motions and laws, so that the distinctive properties of the gaseous state are reduced to a minimum, and matter is thus converted into an ultra-gaseous condition. A similar state will be produced, when by some extraneous force order may be infused into the disorderly jostling of the molecules in gases, by coercing them into some methodical rectilinear movement. Phenomena such as these cause the movements of the radiometer, and the author, in his experiments on negative discharges in vacuum tubes, has rendered such regular motions visible. The gaseous and fourth states of matter merge insensibly into one another, as do the solid into the liquid, or the liquid into the gaseous. These considerations lead to the speculation that the molecule is the only true matter, whilst matter, according to the usual phraseology, connotes nothing more than the effect on our senses of the movements of molecules.

V. H. V.

**Critical State of Gases.** By W. RAMSAY (*Proc. Roy. Soc.*, 30, 323—329).—The author has made a series of experiments on the phenomenon of the critical state of gases first observed by Andrews. Small tubes filled with methyl formate and its vapour (all air being rigorously excluded) were inserted in a heated copper block; it was observed that as the temperature rose the meniscus became gradually less curved, disappearing at  $221.5^{\circ}$ , whilst on cooling to  $218^{\circ}$  a mist was seen at the point where the meniscus had disappeared. In another experiment, two similar tubes were prepared, one containing more, the other containing less of the ethereal salt; in the former, the meniscus disappeared at  $228^{\circ}$ , and in the latter at  $215^{\circ}$ . The experiments were varied by the use of a tube drawn out slightly in the middle, and filled up to a certain mark with methyl formate; and it was found that when the tube was heated and then allowed to cool, the liquid always condensed in that half of the tube in which it was originally contained, even when the position of the tube had been reversed during the experiment. From observations not here detailed it appears probable to the author that the sp. gr. of the hot liquid at the temperature at which the meniscus vanishes is identical with that of the compressed gas evolved from the liquid, so that the critical point may be defined as *that point at which the liquid owing to expansion, and the gas owing to compression, acquire the same sp. gr., and consequently are capable of mixing with one another.* But the refractive index of the fluid contained in that part of the tube which after the vanishing of the meniscus appeared *full*, was different from that in the other half of the tube which appeared *empty*. It is thus possible to retard the admixture of these two fluids so that they both retain their several respective indices. From experiments, the author concludes that the observations of Hannay and Hogarth, on the solubility of solids in gases, are merely cases of the ordinary phenomenon of solubility of solids in liquids. In a postscript to the paper, the author adduces experiments

with carbon bisulphide and tetrachloride, in order to show that the temperature of the critical point varies according to the amount of liquid originally placed in the compression-tube. V. H. V.

**State of Fluids at their Critical Temperature.** By J. B. HANNAY (*Proc. Roy. Soc.*, **30**, 478—484).—The author at the outset makes some remarks on the difference between the liquid and the gaseous state; in the latter the *vis vivâ*, or heat-energy of the molecule, has entirely overcome cohesion or mutual attraction; in the former the attractive power is greater than the *vis vivâ*, and the molecules are enabled to group themselves. The object of the experiment is to decide the question whether, when the temperature of a liquid retained under great pressure is raised, the liquid loses its cohesion and becomes a gas, or, as the pressure is increased, does the temperature rise at which the cohesion of the liquid is overcome. A quantity of hydrogen was introduced over pure alcohol in the compression-tube of a modified Andrews's apparatus in order to obtain a free surface of liquid at any pressure. Then if the temperature is only 1° C. below the critical point, the alcohol boils when the pressure is sufficiently reduced; but if the temperature be 1° above the critical point, the fluid only expands, and boiling is not seen at any pressure from 50—200 atmospheres. In both experiments the fluid had a perfectly free surface. These experiments show that the liquid state comes to an end, and the gaseous state supervenes, quite independently of the pressure. Similar experiments showed that at a few degrees below the critical point the alcohol was undoubtedly liquid, and a few degrees above undoubtedly gaseous. In another series of experiments, the compression-tube was bent at an obtuse angle, and in the lower part was enclosed some dry nitrogen. When the required temperature and pressure were reached a bubble of nitrogen was manipulated round the bend; then if the fluid were in the liquid state, the bubble showed a meniscus, but if gaseous the bubble instantly diffused into the enclosed space. When the temperature was below the critical point the contents of the tube were liquid, but when it was above that temperature they were gaseous.

From these experiments the author concludes that the liquid state ceases at the critical temperature, and that pressure will not materially alter the temperature at which the cohesion limit occurs.

V. H. V.

**The Critical Point of Mixed Vapours.** By J. DEWAR (*Proc. Roy. Soc.*, **30**, 538—546).—The author has made a series of experiments on the liquefaction of carbonic anhydride in the presence of other bodies. When carbonic anhydride was liquefied in presence of a small quantity of carbon bisulphide, it floated on the convex side of the latter, the line of separation being well defined. But on keeping the temperature at 47° C., and increasing the pressure to 110 atmospheres, this line of demarcation had disappeared with formation of a homogeneous fluid; but on again reducing the pressure an upper layer of liquid carbonic anhydride became visible.

Similar results were obtained with carbonic anhydride and chloroform. When carbonic anhydride was liquefied in presence of benzene,



the surface of the latter became violently agitated at the moment of liquefaction, the carbonic anhydride falling through the benzene in an oily stream, and ultimately becoming completely mixed with it. On releasing the pressure, the carbonic anhydride commenced to boil from the bottom of the benzene. With ether similar results were obtained.

When carbonic anhydride was liquefied with other gases, such as nitrous oxide, acetylene, and hydrochloric acid, perfectly homogeneous liquids were formed; and on suddenly withdrawing the pressure, the less condensable of the two fluids boiled before the other. On the liquefaction of carbonic anhydride with camphor at  $15^{\circ}$  and pressure of 27 atmospheres, the latter melted, and ran down the walls of the tube; at rather higher temperatures two distinct liquids were formed, which shortly became homogeneous. These experiments show that carbonic anhydride at high pressures, in presence of various substances, produces a series of unstable chemical compounds, which are decomposed and recomposed according to the conditions of temperature and pressure in the medium.

V. H. V.

**Dissociation of Ammonium Sulphhydrate.** By R. ENGEL and MOITESSIER (*Compt. rend.*, **93**, 730—731).—The authors claim priority over Isambert, on grounds that they started the work in 1879 and have never relinquished it. Wurtz remarked that he had stopped the dissociation of phosphorus pentachloride by diffusing its vapour in that of one of its constituents, phosphorus trichloride (*Compt. rend.*, **76**, 601).

D. A. L.

**Tension of the Vapour of Ammonium Carbamate.** By ISAMBERT (*Compt. rend.*, **93**, 731—734).—In a paper published in the *Compt. rend.* (**93**, 395), Engel and Moitessier make the statement that a dissociable body will not dissociate in presence of one of its products of dissociation at a tension equal or superior to the tension of dissociation, and at the temperature of operation. The author says that this law is more simply expressed thus: if the pressure of the gas is less than the maximum tension in a vacuum, the total tension will be at this maximum, whilst in the opposite case the value will remain the same as that of the free gas. This is not verified by his experiments, either on ammonium sulphhydrate (*loc. cit.*, **92**, 919), where he found at  $15^{\circ}$  the tension of ammoniac sulphhydrate in a vacuum = 259 mm., whilst in gaseous ammonia of tension of 321.2 mm., the total pressure = 421 mm., and in hydrogen sulphide at  $375.8$  mm., the total pressure = 454 mm.; or now, with ammonium carbamate, when he found the following numbers:—

NH <sub>3</sub> CO <sub>2</sub> in vacuo.		In gaseous ammonia.			In carbon dioxide.		
Temp.	mm.	Temp.	Press. NH <sub>3</sub> . mm.	Total press. mm.	Temp.	Press. CO <sub>2</sub> . mm.	Total press. mm.
37·8°	252	21·3°	368·0	376	44·7°	381·3	547
46·9	435	31·9	382·0	412	48·5	385·9	610
49·6	500	39·1	391·0	448	50·5	388·3	656
53·0	601	43·0	395·9	490	52·0	390·0	691
55·6	684	46·4	400·2	550	54·5	393·0	778
59·5	871	50·0	404·7	625	56·6	395·7	840
60·4	918	51·5	406·4	631	59·9	399·5	985
65·1	1206	53·0	408·4	697	61·5	401·5	1056
67·6	1372	55·3	411·3	778	—	—	—
—	—	57·6	414·2	879	—	—	—
—	—	61·0	418·4	1051	—	—	—
—	—	64·1	422·0	1181	—	—	—

which show that the total pressure in presence of an excess of the component gases is always superior to the maximum tension in a vacuum.

D. A. L.

**Influence of Pressure and Temperature on the Surface Condensation of Gases.** By H. KAYSER (*Ann. Phys. Chem.* [2], **14**, 450—468).—This is a continuation of previous work (*Wied. Ann.*, **12**, 526).—No definite results have been obtained, but they were sufficient to show that the phenomena are much more complicated than is generally supposed, and that the laws enunciated by Angus Smith and Weber do not hold good, since the relative values for different gases vary differently with alterations in pressure and temperature. It is also shown that the absorptive power of powdered charcoal is at first less, and afterwards greater than that of larger pieces, and that this is also the case with glass in the form of threads and powder.

T. C.

**Lowering of the Freezing Point of Water by Pressure.** By J. DEWAR (*Proc. Roy. Soc.*, **30**, 533—538).—The author has made a series of quantitative determinations of the lowering of the freezing point of water by means of the Cailletet apparatus. The method of observation was as follows:—A thermo-junction was frozen in a test-tube, which was placed in the iron bottle of a Cailletet apparatus, whilst another thermo-junction outside was maintained at the constant temperature of melting ice. Both thermo-junctions were connected with a galvanometer, the deflections of which were noted and reduced to thermometer degrees. It was found that the freezing point was lowered 0·18° C. for 25 atmospheres, or 2·1° for 300 atmospheres; the mean reduction for one atmosphere is thus 0·0072°. Similar experiments lead to approximately the same results. It appears from the author's experiments that the calculated value of the variation of the freezing point of water, deduced from the observed difference of the volumes of water and ice, and the latent heat of fluidity at the melting point under atmospheric pressure, is identical with the mean experi-

mental value obtained from a series of experiments up to 700 atmospheres. From the formula  $\frac{TV}{L} = \text{constant}$  (T, absolute temperature, V, difference of volume of the two states, L, latent heat of fluidity); then if V is assumed to be constant, T varies as L. Thus the latent heat of ice diminishes as the freezing point is lowered by pressure.

V. H. V.

**Solubility of Solids in Gases.** By J. B. HANNAY and J. HOGARTH (*Proc. Roy. Soc.*, **30**, 178—188, and 484—489).—If the property of dissolving solids is essential to liquids, then on passing through the critical state there should be a precipitation of the solid, but if on the other hand no separation occurs, a further proof is adduced of the continuity of the gaseous and liquid states. The authors, by the use of a modified Andrews's apparatus, have succeeded in dissolving and maintaining in solution potassium iodide in alcohol gas at 300°, or about 70° above the critical point of alcohol. If the pressure is rapidly reduced, the solid is deposited on the wall of the glass tubing in the form of small crystals; on again increasing the pressure, the crystals are redissolved. Similar results are obtained with solutions of potassium bromide and calcium chloride in alcohol. Cobalt chloride remains in solution at 320°, the beautiful blue colour being unimpaired. Selenium also remains in solution in carbon bisulphide, and separates out in part on cooling. The following determinations were made of the critical points of alcohol and of carbon bisulphide and tetrachloride.

	Alcohol.	CS <sub>2</sub> .	CCl <sub>4</sub> .
Temperature.....	234.6	272.96	277.9
Pressure in atmospheres	65	77.9	58.1

These numbers differ slightly from those of Cagniard de la Tour, and the difference is possibly due to the difficulty of rendering alcohol anhydrous. In order to decide the question whether the absorption spectrum of a substance dissolved in a fluid above its critical point differs from that of the substance in liquid solutions or in the solid state, the absorption spectra of cobalt chloride in liquid and gaseous alcoholic solution were compared, and were found to be practically identical. Similar results were obtained with a solution of chlorophyll in gaseous alcohol at 350°. These experiments afford a proof of the perfect continuity of the liquid and gaseous states, and of the solubility of solids in gases.

In the second communication, the authors examine the question whether the critical point of alcohol containing iodine in solution is higher than that of pure alcohol. The following determinations were made:—

	Pure alcohol.	Alcohol containing KI.
Temperature .....	234.3	235.1
Pressure .....	64.5	65.8

The introduction, then, of the solid slightly raises the critical point. The authors have arrived at the following conclusions with regard to

the solubility of solids in gases:—1st. The gas must have a certain density before it will act as a solvent, for when the volume is increased to more than twice the volume occupied by the substance in the liquid state, its solvent power is almost destroyed. 2nd. With constant volume, the higher the temperature the greater the solvent power. The latter conclusion was arrived at by determinations of the solubility of potassium iodide in alcohol at various temperatures. The authors adduce a series of experiments to meet the criticisms of Ramsay, and to prove that the critical point of carefully dried liquefied gas was the same whether observed at the bottom or top of the tube. But using organic substances, which cannot be completely purified, as ethyl and methyl oxalates, there was a difference of several degrees in the critical point if the observation was taken at the top or bottom of the tube. Finally, if, as Ramsay suggests, the solubility of solids in gases, as observed by the authors, is nothing but the ordinary phenomenon of solution of solids in liquids, then the solid, not being soluble in the gas, would be precipitated when the liquid mixed with the gas, just as a substance is precipitated when a solution of it is mixed with another liquid in which it is insoluble. The authors, moreover, find not the slightest difference in refractive power of the upper and lower layers of compressed fluid in the tubes. Solution of solids is then a function of all fluids, the requisite condition being molecular closeness and thermal activity.

V. H. V.

**Absorption of Gases by Solids.** By J. B. HANNAY (*Proc. Roy. Soc.*, 32, 407—408).—In the course of the separation of crystalline carbon from its compounds, the author observed that the iron tubes, after being heated in the furnace, were found to be emptied of their contents, although testing by hydraulic pressure showed no leakage. As the gases seemed to pass through the solid iron, various siliceous linings were tried without success. In order to examine the question whether solid matter at high pressure and temperature is pervious to gases, preliminary experiments were made on the absorption of oxygen and carbonic anhydride by glass at 200° under a pressure of 200 atmospheres. It was found that so much gas was absorbed and permanently retained, that if the glass, after being cooled under pressure, is quickly heated to its softening point, the sudden escape of gas drives the glass into foam. Similar results were obtained with other silicates, and also with borates and phosphates; metals also absorb hydrogen and some of its compounds with carbon.

V. H. V.

**Specific Viscosity of Liquids.** PART III. By R. PRIBRAM and A. HANDL (*Monatsh. Chem.*, 1881, 643—715).—The specific viscosity of isomeric ethereal salts is not identical. As a rule, the difference between the viscosity of equal volumes of the isomeric ethereal salts increases with the molecular weights of the compounds. Substances containing normal alcoholic or acid radicals generally have a greater viscosity than the corresponding iso-compounds. The butyl alcohols, nitrobutanes and propyl chlorides, bromides and iodides, form an exception to this rule. When an alcohol is converted into an aldehyde or ketone, a great diminution in specific viscosity is observed. At 10° the

decrease (for equal volumes) is equal to 0·843 per cent. of the specific viscosity of the alcohol. The absolute difference between the specific viscosities of homologous alcohols and their corresponding aldehydes and ketones increases with the molecular weight of the compounds.

In homologous series, the increase in viscosity is proportional to the increase in the molecular weight, but the coefficient depends on the structure of the molecule. The butyl alcohols form an exception to this rule.

W. C. W.

**Researches on the Welding of Solid Bodies induced by Pressure.** By W. SPRING (*Bull. Acad. Belg.*, 1880 [2], 49, 323—379; Abstr., *Jahrb. f. Min.*, 1882, 1, Ref., 42—45).—The phenomenon exhibited in the regelation of ice may, under favourable circumstances, be produced in other bodies, as in the caking together of pulverised sodium nitrate. The conditions necessary for effecting this cohesion are pressure, a suitable temperature, and time. Coarsely powdered sodium nitrate, under ordinary pressure, shows but little tendency to cake together, the number of points of contact between the particles not being sufficient to induce cohesion; but on subjecting the powder to increased pressure, the particles are brought within each other's sphere of cohesion, and then unite like drops of water. The cohesion, or welding, thus produced is, to a certain extent, analogous to the liquefaction of a gas by pressure.

The apparatus used by the author was capable of exerting a pressure of about ten thousand atmospheres, and experiments were made with it on various metals at high pressures and at the temperature of 14°.

Lead-filings, under a pressure of 2000 atm., were compressed into a uniform block, which, under the microscope, exhibited no trace of the original filings, but looked just like a block of cast lead: sp. gr. = 11·5013. At a pressure of 5000 atm. the lead oozed out at all the joints of the apparatus as if it were liquid, in the same manner as in Tresca's well-known experiments on the flow of solid bodies. Bismuth in fine powder, under 6000 atm., was converted, as if it had been fused, into a uniform block having a crystalline fracture and sp. gr. = 9·8935. Tin filings, at 3000 atm., behaved like lead and bismuth; at 5000 atm. the metal began to ooze out at the joints; the flow, however, soon ceased; began again at 5500 atm.; again ceased; was renewed at a higher pressure, and so on up to 7500 atm., at which the flow became continuous. Zinc-filings were completely welded at 5000 atm., the change taking place more readily at a temperature of 130°, the block having then a crystalline fracture. Aluminium-filings weld perfectly at 6000 atm., and the metal (sp. gr. = 2·5615) begins to become plastic. Copper behaves like aluminium. Antimony in fine powder, black and destitute of metallic lustre, yields at 5000 atm. a block having a metallically lustrous surface, but still pulverulent and dull-grey in the interior. As the pressure is increased, the metallic lustre penetrates further and further inwards. In like manner in all the experiments, the action does not take place suddenly, but increases steadily with increasing pressure till it becomes complete. Platinum-sponge gave, at 5000 atm., a block having a shining metallic surface, but still friable and exhibiting

a dull fracture. Increased pressure, however great, did not, as with the other metals, give rise to perfect union. These experiments demonstrate the interesting fact that the capacity of metals to weld into compact masses under high pressure is inversely proportional to their hardness; and since hardness, as a rule, diminishes with rise of temperature, it may be assumed that the property in question will increase with rise of temperature in metals the more they soften when heated. Iron, which softens very much when heated, is well known to weld with great facility.

Among non-metallic bodies, sulphur, phosphorus, and carbon were subjected to experiment. Monoclinic sulphur, at 5000 atm. pressure, unites into a compact block, harder than sulphur which has been fused, melting at  $115^{\circ}$ , and of sp. gr. 2.0156. Now monoclinic sulphur has a density of 1.96, and melts at  $120^{\circ}$ , whereas rhombic sulphur has a density of 2.05, and melts at  $111-114^{\circ}$ ; hence the author infers that monoclinic sulphur is converted by pressure into the rhombic modification. Plastic sulphur bears, without immediate alteration, a pressure of 3000 atm., but at 5000 atm. it becomes covered with a brittle crust of rhombic sulphur, the interior still remaining plastic, and at 6000 atm. the whole becomes converted into rhombic sulphur. Hence the author infers that when a body susceptible of allotropic modifications has its density increased by pressure, it assumes that modification which corresponds with the increased density. Of the other experiments with metalloids, it is sufficient to notice that amorphous carbon, obtained by calcination of sugar, gave absolutely negative results, even under the highest pressure, whereas graphite-powder, as is well known, is converted at 5500 atm. into a compact mass having the same degree of solidity as native graphite.

Among the experiments with oxides, it may be noticed that the artificially prepared brown powder of manganese dioxide, under a pressure of 5000 atm., is converted into a black hard block exhibiting a crystalline fracture, and undistinguishable from native pyrolusite. Alumina, obtained by precipitating aluminium sulphate with ammonium carbonate and drying at  $140^{\circ}$ , becomes, at 5000 atm., compact, translucent, and similar in colour to halloysite, but flows at the same time like a liquid. Experiments with silica, native and artificial, gave no result, on account of the great hardness of this body. Charcoal powder, either meagre or fat, is compressed at 6000 atm. to a compact lustrous block, perfectly kneadable at that pressure: whereas charcoal, at ordinary pressure, is extremely brittle. Dutch peat from the province of Drente, and Belgian peat from the neighbourhood of Spaa, having a brown colour and mixed with much vegetable fibre, were converted, at 6000 atm., into black, shining, hard blocks, having exactly the appearance and laminated structure of coal; the organic texture had completely disappeared, and the peat had become plastic throughout.

Another series of experiments relates to the influence of pressure on the course of chemical reactions. On comparing the sums of the volumes of two bodies before and after they have acted on one another, it appears that chemical processes may be divided into two classes,

viz., those in which the volumes of the reacting bodies increase, *e.g.*,  $\text{CaCO}_3 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + \text{H}_2\text{O} + \text{CO}_2$ , and those in which they decrease, *e.g.*,  $\text{CaO} + \text{CO}_2 = \text{CaCO}_3$ , the pressure of course being supposed to remain constant. The experiments of Cailletet and of Pfaff (*Jahrb. f. Min.*, 1871, 837) have shown that a pressure of 60—120 atm., is sufficient to render actions of the first kind impossible. Actions of the second kind, on the other hand, are facilitated by pressure, as Spring's experiments show. Thus copper-turnings and coarsely powdered sulphur unite, under 5000 atm., to black crystalline copper-glance. A coarse mixture of mercuric chloride and copper-filings is converted, under the same pressure, into cupric chloride and metallic mercury, no cuprous chloride being formed. When a white mixture of dry potassium iodide and mercuric chloride is subjected to a pressure of 2000 atm., a red block is obtained consisting of mercuric iodide and potassium chloride, in which every trace of white substances has disappeared, as if one of the salts had soaked into the other. A mixture of potassium iodide and mercuric sulphide subjected to pressure, yielded a compact block, but no chemical reaction appeared to take place. Neither was chemical action distinctly perceived on pressing a mixture of ferrous sulphide and sulphur, or of mercuric oxide and sulphur. When an intimate mixture of tartaric acid and dry sodium carbonate was pressed, not a trace of carbonic anhydride was evolved, but a mixture of sodium carbonate and arsenic oxide under pressure yielded sodium arsenate, with copious evolution of carbonic anhydride.

The results of these experiments have an important bearing on many geological phenomena, showing that the solid state of aggregation depends, not only on temperature, but also on pressure, and that solid, even very brittle bodies may acquire under high pressure, without elevation of temperature, a high degree of plasticity—a fact of the highest importance for the theory of rock-formation. They further show that high pressure is an important factor in chemical action, and thus afford an experimental basis for the conception of a mechanical metamorphosis. H. W.

**Molecular Volume of Solids.** By E. WILSON (*Proc. Roy. Soc.*, 32, 457—491).—The author in this paper has collated a series of tables of specific gravities of solids, in order to trace the relation between molecular volume and chemical constitution. An element does not carry its atomic volume unchanged into its compounds, nor is it even probable that there can be assigned to an atom of a compound molecule a particular volume exclusive of that occupied by the remaining atoms in the molecule; although, as each atom plays a certain part in the formation of the common volume, a certain fraction of that volume may be attributed to it. The atomic volume of each element can thus be deduced from a comparison of the sp. gr. of those compounds in which that element is a constituent. In order to solve the question of the relations which obtain between the molecular volume of a solid and the particular volume of each of its components in the so-called free state, the author enunciates the following propositions:—

(i.) When any number of *similar* atoms combine, the volume of the resulting molecule is equal to that of the uncombined atom.

(ii.) When dissimilar atoms combine, the volume assignable to each atom is some simple submultiple or aliquot part of its atomic volume, and the resultant molecular volume is the sum of these volumes.

(iii.) Every element in its various compounds is capable of assuming different volumes bearing a simple proportion to one another, such as 1 : 2, 1 : 3, 2 : 3, &c.

In order to trace out the evidence which is brought forward in support of these views, an explanation of the methods, and illustration of them, may be given. The number to be assigned to the molecular or atomic volume of each element is always some multiple of its atomic weight divided by its sp. gr.; but an examination of its compounds is required in order to determine what particular multiple it must be. Thus the atomic weight of sodium, divided by its sp. gr., is 24, and an examination of its compounds shows that this element assumes the volumes 8, 12, or 24; 2 is therefore the proper multiple, and the fundamental number to be assigned to sodium is 48. Similarly, the atomic weight of boron, divided by its sp. gr., is 4: its volume in its compounds is 7 or 14: whence 7 is the proper multiple, and 28 the fundamental number of boron. Such atomic volumes are represented by symbols Na', B', or K', while Na''<sub>3</sub>, K''<sub>3</sub> are expressions for the molecular volume of any substance containing potassium or sodium, and mean that the volume to be ascribed to these elements in any particular molecule is found by dividing the fundamental number by 3, and multiplying the quotient by the number of atoms in that molecule. Thus the fundamental numbers of potassium, sulphur, and oxygen are 90, 96, and 20, and the expression for its molecular volume is K''<sub>6</sub>S''<sub>6</sub>O''<sub>4</sub>, which means that the number K' = 90 has to be divided by 6, and then multiplied by 2; the number S' = 96 to be divided by 6, and the number O' = 20 to be divided by 4, and the quotient multiplied by 4. Thus the sum of the resultant number (30 + 16 + 20) = 66, is the molecular volume of potassium sulphate, and its sp. gr. (or molecular weight divided by molecular volume) is  $\frac{174}{66} = 2.636$ ,

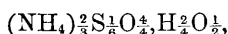
which agrees with its observed value, 2.64. In the series of tables, the calculated specific gravities of various elements and their compounds, as oxides, chlorides, nitrates, sulphates, &c., are compared with the observed specific gravities. According to proposition (1) an explanation is given of the different specific gravities of allotropic modifications of elements and of compounds which, although of the same chemical composition, yet possess two or more distinct specific gravities; these differences being due to the different number of atoms contained in the respective molecules. In the tables below, a few such examples are collected to illustrate the agreement between the calculated and observed specific gravities:—



Element.	Atomic weight.	Molecular weight.	Molecular volume.	Calculated sp. gr.	Observed sp. gr.
C (diamond) ....	12	C <sub>9</sub>	32	3·375	3·35
C (graphite) ....	"	C <sub>6</sub>	"	2·25	2·25
C (lamp-black) ..	"	C <sub>5</sub>	"	1·875	1·885
Si (graphitoidal)..	28·5	Si <sub>6</sub>	70	2·443	2·49
Si (amorphous) ..	"	Si <sub>5</sub>	"	2·035	2·00
P (red) .....	31	P <sub>7</sub>	102	2·127	2·14
P (yellow) .....	"	P <sub>6</sub>	"	1·823	1·83
P (white) .....	"	P <sub>5</sub>	"	1·519	1·515

Compound.	Molecular weight.	Molecular volume.	Calculated sp. gr.	Observed sp. gr.
Silicon dioxide (amorphous).	SiO <sub>2</sub>	Si $\frac{1}{4}$ O $\frac{3}{4}$	2·2	2·2
" (crystalline) .	"	Si $\frac{1}{4}$ O $\frac{3}{4}$	2·688	2·69
Titanium dioxide (rutile) ..	TiO <sub>2</sub>	Ti $\frac{1}{4}$ O $\frac{3}{4}$	4·256	4·250
" (cinastase)	"	Ti $\frac{1}{4}$ O $\frac{3}{4}$	3·875	3·89
Mercury sulphide (cinnabar)	HgS	Hg $\frac{1}{4}$ S $\frac{3}{4}$	7·606	7·552
" (amorphous)	"	Hg $\frac{1}{4}$ S $\frac{3}{4}$	9·027	8·998

Evidence is also brought forward in support of the original conjecture of Kopp, that an element in the same compound may undergo different degrees of condensation, if it enters into the composition of two distinct radicles. Hydrated ammonium sulphate affords an example of this: its molecular volume may be expressed by a formula,



in which the hydrogen in the ammonium radicle is condensed to one-third, but in the water of crystallisation to one-fourth, and the oxygen atom in the acid radicle is condensed to one-fourth, but in the water to one-half.

The author also points out the agreement between the results obtained by his theory and those obtained by Loschmidt from observations on the interdiffusion of gases.

In conclusion, the author remarks that the tables lend comparatively greater support to proposition (iii), whilst propositions (i) and (ii) must, for the present, be considered more hypothetical.

V. H. V.

## Inorganic Chemistry.

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**Preparation of Chlorine and Hydrochloric Acid.** By E. SOLWAY (*Dingl. polyt. J.*, **242**, 287).—For the preparation of dry hydrochloric acid, the author recommends to pass a mixture of hydrochloric acid, steam, and other gases into a concentrated solution of calcium chloride, which retains hydrochloric acid and water. On warming this mixture, dry hydrochloric acid gas is evolved. A similar result is obtained by the addition of calcium chloride to commercial hydrochloric acid, and subsequently heating the mixture. The author further proposes to prepare chlorine and hydrochloric acid from calcium chloride by heating the latter with silicic acid or aluminium silicates, and passing a current of air or steam over the mixture. The residue is worked up for cement by mixing it with clay or lime in proper proportions. D. B.

**Variations of the Amount of Oxygen in the Atmosphere.** By E. W. MORLEY (*Sill. Am. J.* [3], **22**, 417—428).—Two series of daily determinations of the oxygen in the air at Hudson, Ohio, have been made from January 1st to June, 1880, and from October 1st, 1880, to April 20th, 1881; by comparing them with the temperature and pressure, it is seen that in some cases, where the meteorological conditions of the region are simple, the deficiencies in the proportion of oxygen follow closely on periods of high pressure and low temperature, when it would be natural to suppose that currents of air from high regions are descending. There is very little in the results to lead to any connection between the direction of the wind at the time of taking the sample and the deficiency of oxygen.

The results are tabulated, and numerous comparisons made between the deficiency in oxygen and the pressure, temperature, and direction of the wind. L. T. O'S.

**Jolly's Hypothesis as to the Cause of the Variation in the Proportion of Oxygen in the Atmosphere.** By E. W. MORLEY (*Sill. Am. J.* [3], **22**, 429—434).—This is a criticism of Jolly's hypothesis, that the variation in the ratio of oxygen to nitrogen in the atmosphere is due to currents of air coming from the tropics, where the consumption of oxygen by the oxidation of organic matter is in excess of that liberated by the process of vegetation. L. T. O'S.

**Silica and Lithium Silicates.** By P. HAUTEFEUILLE and J. MARGOTTET (*Compt. rend.*, **93**, 680—689).—Three silicates are described. The silicate,  $\text{SiO}_2 \cdot 2\text{Li}_2\text{O}$ , similar to peridot, crystallises in prisms (pseudo-hexagonal derived from orthorhombic prism), is transparent and colourless, or slightly amber-coloured. By contact with water, it became flinty in appearance, on account of a superficial alteration; on boiling for some time, a notable quantity of lithia and silica is dissolved. The silicate,  $\text{SiO}_2 \cdot \text{Li}_2\text{O}$ , crystallises from lithic chloride in long flat prisms, sometimes terminating in symmetrical

domes; they are six-sided, and are derived from orthorhombic prisms. The silicate,  $5\text{SiO}_2, \text{Li}_2\text{O}$ , forms flexible laminæ (orthorhombic), having in all five cleavages, one in direction of the greatest length, one perpendicular to it, one parallel to the plane of the laminæ, and two others, difficult ones, which furnish thin rhombic plates. The first two silicates are attacked by acids; the last one resists their action. They are all difficult to fuse; but become very fluid when heated to high temperatures, dissolving a great deal of gas, which they give up again on solidifying. The authors have crystallised five different specimens from fused lithium chloride, and have established the fact that silica can take the form of quartz in presence of a fused chloride. Lithium chloride alone does not effect this change well; but when a small quantity of oxychloride is mixed with it, the crystallisation takes place easily. Lithium chloride abstracts the lithia from the silicates of lithia to form the oxychloride. D. A. L.

**Revision of the Atomic Weight of Aluminium.** By J. W. MALLETT (*Proc. Roy. Soc.*, **30**, 329—332, and 574—576).—The author has re-determined the atomic weight of aluminium by three separate processes: firstly, by igniting a known weight of ammonium alum, and weighing the alumina formed; secondly, by precipitating a solution containing a known weight of aluminium bromide with a standard silver nitrate solution; thirdly, by dissolving a known weight of aluminium in sodium hydroxide, and measuring the volume of hydrogen given off, or burning it and weighing the water produced. The author considers that of these three processes the first is the least exact, owing to the gradual loss of water which crystallised ammonium alum undergoes when exposed for some time to the air; whilst the last, owing to its simplicity, is probably the most exact. The mean of the experiments, thirty in all, is  $\text{Al} = 27.032$ , with a probable error of  $\pm 0.0045$ ; whilst, excluding some of the determinations by the first method, in which the alum was dried by exposure to the air for 24 hours, the mean result of the remaining determinations is  $\text{Al} = 27.019$ , with a probable error of  $\pm 0.0030$ . Aluminium is therefore another of the elements whose atomic weight is found to approximate closely to an integer. The author also draws attention to the fact, that of the eighteen elements whose atomic weight may be considered to be accurately determined, nine have an atomic weight within 0.1 of an integer. The probability of this, according to the theory of chances, is 1 in 235.2. It thus appears that not only is Prout's law not absolutely overthrown, but that the evidence in its favour, or in favour of some modification of it, is gradually increasing and requires consideration.

In the second communication, the author examines the possible source of error due to the occlusion of hydrogen by metallic aluminium, as observed by Dumas, but it was found that the greatest error in the volume of hydrogen derived from this source would affect the atomic weight to an extent less than one-tenth of the probable error of the mean result. Hence it appears that, although the error is constant, yet its influence is inappreciable.

V. H. V.

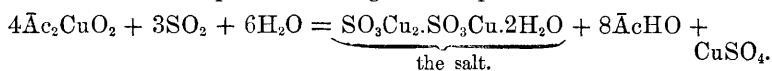
**Hydrated Chromium Bromide.** By L. VARENNE (*Compt. rend.*, **93**, 727—728).—When silver chromate is treated with hydrobromic acid, a hydrated chromium bromide is formed; it is soluble in water, and is left in green crystals on evaporation. When a cold concentrated solution of potassium trichromate is treated with dilute hydrobromic acid, bromine is evolved, the solution turns brown, and if left to itself in the cold at about 0°, it deposits violet crystals (cubic octohedrons) of  $\text{Cr}_2\text{Br}_3 + 16\text{H}_2\text{O}$ , soluble in water to a green solution. At 110° they lose their water, becoming green; at 200°, in the air, they give a clear green oxybromide, which is ultimately converted into chromic oxide.

D. A. L.

**Action of Hydracids on Alkaline Chromates.** By L. VARENNE (*Compt. rend.*, **93**, 728—730).—Trichromates, when treated with hydrochloric acid, yield chromium chloride, and a body of the formula  $\text{CrO}_2\text{Cl}_2$ ,  $\text{CrO}_3\cdot\text{MO}$  or  $2\text{CrO}_3\cdot\text{MCl}_2$ , according to the constitution assigned it, chlorine being evolved at the same time. Hydrobromic and hydroiodic acids act in a like manner. Hydrofluoric acid acts differently; for if this acid is added to a concentrated solution of ammonium trichromate in nitric acid, the mixture moderately warmed, and then left to itself, beautiful brilliant red needles separate out. They are efflorescent, attack glass, evolve hydrofluoric acid and deposit chromic acid when treated with an acid, are instantly decomposed by water, and on heating they leave a residue of chromic oxide; the analytical results correspond with the formula  $2\text{CrO}_3\cdot\text{F}_2\text{CrO}_3\cdot(\text{NH}_4)_2\text{O}$ .

D. A. L.

**Cuprosocupric Sulphite.** By A. ÉTARD (*Compt. rend.*, **93**, 725—727).—By passing a rapid current of sulphurous anhydride through a solution of cupric acetate (77 grams to the litre) kept at 65°, a sandy crystalline precipitate is formed of a salt discovered by Chevreul. The reaction takes place according to the equation:—



This salt is probably a double salt of cuprous with cupric sulphite. Heated at 180° in a closed tube with sodium bisulphite or sulphurous acid, or with distilled water, it is converted into sulphuric acid and crystalline metallic copper. Heated to the same temperature in a current of sulphurous anhydride or of carbonic oxide or anhydride, the salt loses 26 per cent. of its weight, and leaves a crystalline basic sulphite,  $\text{SO}_3\text{Cu}_2\text{CuO}$ . The volatile products at this temperature are always water and sulphurous anhydride. It is decomposed by hydrogen sulphide, forming  $\text{Cu}_3\text{S}_2$ . In carbonic anhydride at a red heat, equal molecules of  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  are obtained.

D. A. L.

## Mineralogical Chemistry.

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**Artificial Formation of the Diamond.** By J. B. HANNAY (*Proc. Roy. Soc.*, 30, 188—189, and 450—461).—In these papers an account is given by the author of the successful and unsuccessful attempts to obtain carbon in the crystalline state by artificial processes. It was found that when the alkali-metals, preferably lithium, were heated with paraffin hydrocarbons, carbon is deposited in hard scales. The author states that in an experiment, in which lithium was heated with a mixture of 90 per cent. bone-oil and 10 per cent. paraffin spirits in a coil-iron tube to a visible red heat for 14 hours, a hard smooth mass was found at the bottom of the tube, containing hard transparent particles imbedded in it. The particles, consisting of 97·85 per cent. carbon, were identical in chemical and physical properties with the diamond; they were in the octohedral form (sp. gr. 3·5), scratched all other crystals, and had no action on polarised light.

V. H. V.

**Artificial Würtzite.** By H. FÖRSTNER (*Zeitschr. f. Kryst.*, 5, 1881, 363; (*Jahrb. f. Min.*, 1, Ref., 32).—The crystals were found as a furnace-product (locality not stated) on charcoal; they were about 1 mm. long, mostly transparent, with a strong diamond lustre; they belong to the hexagonal system, and are found by qualitative analysis to consist of ZnS: therefore würtzite. They are prismatic, dihexahedral, or terminated by the basal face. Observed faces  $\infty P$ , 2P, 0P,  $\frac{4}{3}P$ . They are hemimorphous, the faces 2P and 0P occurring at one end, while at the other 2P and  $\frac{4}{3}P$  succeed one another in alternate steps: the terminal summit is here also truncated by 0P. The crystals are developed similarly to those of greenockite. Axial ratio  $a : c = 1 : 0·8002$ . Angle  $0P : 2P = 118^\circ 25'$ ;  $\infty P : 2P = 151^\circ 35'$ ;  $2P : 2P = 127^\circ 53'$ ;  $\infty P : \infty P = 119^\circ 58'$ ;  $0P : \frac{4}{3}P = 145^\circ 16'$ . These values differ somewhat from those given by Friedel for natural würtzite, perhaps on account of isomorphous admixtures in the latter. A plate cut parallel to the axis showed the characters of weak double-refracting positive crystals.

H. W.

**Note on Erythrozincite.** By A. DAMOUR; **Note on the Optical Properties of Erythrozincite, Raimondite, and Copiapite.** By A. DES CLOIZEAUX (*Jahrb. f. Min.*, 1882, 1, Ref., 17).—*Erythrozincite* is the name given by Damour to a mineral, consisting essentially of sulphur, zinc, and manganese, occurring in thin red transparent plates in the clefts of a Siberian lazurite. It is soft, and yields a light yellow powder; dissolves in nitric acid, with separation of a small quantity of sulphur which cakes together, yielding a solution in which zinc and manganese can be detected: it likewise exhibits the manganese reaction with phosphorus salt, especially after addition of nitre. According to Des Cloizeaux, who regards the mineral as a manganiferous würtzite, it cleaves in only one direction, which

appears, from the optical phenomena exhibited by the crystal, to be basal: the same phenomena show that the mineral belongs to the optically uniaxial system, and from its analogy to würtzite it is very probably hexagonal.

Breithaupt's *raimondite* is, according to Des Cloizeaux, a hydrated ferric sulphate, not identical with coquimbite. It crystallises in the hexagonal-rhombohedral system, the small lamellæ with hexagonal outline indicating the combination of the rhombohedron with the end-face. Optically they are uniaxial with negative double refraction (coquimbite is uniaxial positive). Sometimes distorted appearances are observed, due probably to overlapping of the layers.

Copiapite is found by Des Cloizeaux, as formerly by Bertrand, to belong to the rhombic system, the fundamental prism having an angle of about  $182^\circ$ . According to Des Cloizeaux, however, the median line normal to the base is negative, and must be regarded as the second. Dispersion of the axes  $\rho < v$ .  $-2H_r = 113^\circ 10\frac{1}{2}'$ ;  $2H_g = 114^\circ 15'$ . The dispersion of the axes is very bright; double refraction strong. On account of the perfect cleavability parallel to the base, it was impossible to obtain a plate parallel to  $\infty P\infty$ , and therefore at right angles to the positive median line.

H. W.

**Crystals of Linnæite found in the Coal-beds of the Rhondda Valley, Glamorganshire.** By W. TERREIL and A. DES CLOIZEAUX (*Bull. Soc. Min. de France*, 1880, **3**, 170; *Jahrb. f. Min.*, 1882, **1**, Ref., 19).—These crystals exhibit the usual form of linnæite (cobalt-nickel pyrites) namely, a combination of the regular octohedron (predominant) with the cube (subordinate). They are very small ( $\frac{1}{2}$  to  $\frac{3}{4}$  mm. in diameter), and grouped and intergrown in irregular masses. They are found in the cavities of a yellowish ankerite (12—14 per cent. FeO), accompanied by millerite, copper pyrites, blende, and galena.

According to Terreil's investigation, made with small quantities of substance, linnæite contains 40 per cent. cobalt nickel and iron, and 3 per cent. copper. (This amount of metal is too small for linnæite.)

The ankerite containing the minerals above mentioned is found, together with blackish carbonate of iron, as filling material of a ferruginous clay, which occurs in the coal-formation in the forms of large flattened kidney-shaped lumps, after the manner of fissured septaria.

H. W.

**Artificial Pseudomorphosis of Calcium Carbonate after Gypsum.** By A. DAMOUR (*Bull. Soc. Min. de la France*, 1880, **3**, 6; *Jahrb. f. Min.*, 1882, **1**, Ref., 32).—When crystals of gypsum are left in a cold saturated solution of ammonium carbonate, ammonium sulphate and calcium carbonate are formed; if the gypsum crystals are only 2—3 mm. thick, the transformation takes place in a few days. Anhydrite, cælestine, and anglesite, in crystals, resist this action much longer than gypsum, but lose their power of resistance when finely pulverised. Barium sulphate resists it altogether.

The carbonates of potassium and sodium, as previously shown by H. Sainte-Claire Deville, act in the same manner as carbonate of ammonium.

H. W.

**Chromophosphate of Lead and Copper.** By F. PISANI (*Bull. Soc. Min. de France*, 1880, **3**, 196; *Jahrb. f. Min.*, 1882, **1**, Ref., 22).—On specimens of vauquelinite from Beresowsk there was found a very small quantity of a dark orange-red mineral in warty forms, having a crystalline structure on the surface. Its analysis gave—

PbO.	CuO.	CrO <sub>3</sub> .	P <sub>2</sub> O <sub>5</sub> .	
70·60	4·57	15·80	9·78	= 100·75

whence the author deduces the formula  $\text{Pb}_3\text{P}_2\text{O}_8, (\text{Pb}, \text{Cu})\text{CrO}_4$ , and places the mineral near Nordenskiöld's laxmannite, Hermann's phosphochromite, and a similar mineral analysed by John. It is distinguished from laxmannite by its colour, and from the last-mentioned mineral by its composition, which approximates most nearly to that of Hermann's phosphochromite. H. W.

**Mimetesite from Laangban.** By W. LINDGREN (*Jahrb. f. Min.*, 1882, **1**, 21).—Mimetesite of blackish-violet colour inclining to rose-red occurs at Laangban, associated with hausmannite, in a mixture of manganese-hornblende and calcite with small quantities of mica and berzeliite. Analysis gave the results cited under I; the quantities of pure arsenates, phosphates, and chlorides calculated therefrom are given under II; whilst III shows the composition of a mimetesite from Johanngeorgenstadt analysed by Wöhler.

	I.		II.	III.
Lead oxide .....	52·02			
Lime .....	12·50			
Zinc oxide .....	1·55			
Manganous oxide ..	1·11			
Alumina, with trace		Lead arsenate....	82·63	82·74
of ferric oxide ..	1·04	Lead phosphate ..	5·21	7·50
Arsenic oxide .....	15·46	Calcium arsenate	1·65	—
Carbon dioxide ....	10·99	Lead chloride....	10·50	9·60
Chlorine .....	1·88		<hr/>	<hr/>
Phosphoric oxide ..	0·64		99·99	99·84
Silica .....	0·94			
Hygroscopic water..	1·63			
	<hr/>			
	99·76			

This mineral exhibits the physical properties of normal mimetesite, excepting that the sp. gr., 5·85, is a little lower than usual, in consequence, no doubt, of the large admixture of carbonates (25·64 per cent.).

The amount of calcium arsenate shows that mimetesite cannot be distinguished with certainty from hedyphane. Under the microscope, the greater part of the mineral appears to be made up of somewhat turbid prisms, exhibiting transverse separation, and a direction of extinction indicative of the hexagonal system. Remarkable also is the exclusively prismatic cleavage, whereas in most specimens of mimetesite and hedyphane, pyramidal cleavage is much more distinct than the prismatic. H. W.

**Mineralogical Notices.** By A. v. LASAULX (*Zeitschr. f. Kryst.* 5, 326; (*Jahrb. f. Min.*, 1882, 1, Ref., 12—16).—1. *On some Minerals from Etna.*—(a.) Cyclopote. This mineral occurs in cavities of the dolerite of the Cyclopean Islands in innumerable small tablets, associated with analcime and needles of augite. In crystalline form and chemical composition it agrees exactly with anorthite. Some of the crystals are perfectly limpid, but the greater number are of a dull white colour, and slightly translucent to opaque.  $H. = 6$ . Sp. gr. = 2.682.

(b.) Analcime. The ordinary form of the transparent and colourless analcime crystal of the Cyclopean Islands is  $\infty O \infty . 2O2$ . The existence of innumerable fissures in the interior of these crystals, while the external portions are free from them, is probably due to internal tension; this is likewise indicated by the optical characters of the crystals, which are doubly refractive.

(c.) Mesolite, Natrolite, Thomsonite. In the cavities of basaltic conglomerates, and in the palagonite tufa of the neighbourhood of Trezza and Aci-Castello, there occur radiofibrous spheres and hemispheres, having their fibres terminated by the face of a nearly square pyramid, and cleavable parallel to  $\infty P$ , one of the cleavage-surfaces being, however, smoother than the other. In true natrolite, the direction of extinction of a polarised ray is perpendicular to the prismatic edge; in true scolerite it is inclined thereto at an angle of  $8^\circ$ — $13^\circ$ ; in the needles under consideration, this inclination is only  $2^\circ$ — $3^\circ$ . According to Sartorius, the mineral is a calciferous natrolite, containing only 1.73 per cent.  $CaO$  to 12.23  $Na_2O$ . V. Lasaulx is of opinion that these and other similar minerals (mesolite, &c.), are isomorphous mixtures of sodium and calcium silicates, and that renewed chemical and optico-crystallographic examination would show the existence of a series analogous to that of the plagioclastic feldspars.

This group of mixed zeolites would also include thomsonite, which occurs, together with the mesolites above mentioned, in the form of transparent colourless prisms, with pyramidal end-faces, and likewise forms spherical aggregates. This mineral has also a direction of extinction inclined  $5^\circ$  to the prismatic edge, and exhibits two different cleavage-faces, one of which has a more distinct nacreous lustre than the other, especially after heating. Cyclopean thomsonite cleaves parallel to the prismatic faces, whereas in thomsonite from the Seeberg, near Kaden in Bohemia, the direction of cleavage is diagonal, showing that the two minerals are essentially distinct; and that the thomsonite of Aci-Castello should be classed with the mesolites.

(d.) Herschelinite. This mineral is found on Etna, near Aci-Castello, in pseudohexagonal forms, viz., six-sided prisms, with arched or rarely with plane end-face. The prismatic faces are formed by the edges of numerous superposed tablets, which also appear to be strongly twisted together round the vertical axis. Optical examination shows that the crystals are monoclinic, the individual crystals being bounded by the orthopinacoid (apparently  $\infty P$ ) and the plane of symmetry (apparent base). The twin-plane appears to be the clinopinacoid, which is inclined  $60^\circ$  to the orthopinacoid. The twin-axis is normal to the



base. The plane of the optic axes is perpendicular to the clinopinacoid, and inclined to the principal axis at  $7^\circ$ .

The analysis of this herschelite gave 57.15 per cent.  $\text{SiO}_2$ , 21.42  $\text{Al}_2\text{O}_3$  (+  $\text{Fe}_2\text{O}_3$ ), 5.34  $\text{CaO}$ , 6.69  $\text{K}_2\text{O}$  (by diff.), and 19.40  $\text{H}_2\text{O}$ , agreeing nearly with that of Sartorius, and leading, according to the author, to the formula  $(\text{Na}, \text{K})_2\text{SiO}_3, \text{CaSiO}_3, 2\text{Al}_2\text{Si}_3\text{O}_9 + 12\text{H}_2\text{O}$ , which v. Lasaulx regards as identical with that of chabasite.

2. *Albite from Monte Cani in the Pyrenees*.—The crystals, from 1—2 mm. to 5 mm. in size, are here found imbedded in a dolomitic limestone, and are developed in the same manner as the albites of Roc-Tourné in Savoy, described by G. Rose. They are associated with many-faced crystals of pyrites, which are combinations of the pentagonal dodecahedron with the cubo-octohedron and diakis-dodecahedron.

3. *A Fossil Resin from the Coal-beds of Upper Silesia*.—This resin, found in the Napoleon mine at Mockrau and in the Burghard and Albert mines at Nicolai, Circle of Pless, contains, according to an analysis by Ladenburg, 80.56 per cent. carbon, 6.30 hydrogen, 12.68 oxygen, and 0.46 ash, agreeing with the formula  $\text{C}_9\text{H}_8\text{O}$ . It lies upon coal, and is intimately combined therewith. It melts easily with some degree of tumefaction, and burns with a yellow, very smoky flame, emitting an aromatic odour. Ether dissolves the greater part of it, leaving only a very small black pulverulent residue.

H. W.

**On Analcime.** By A. BEN-SAUDE (*Jahrb. f. Min.*, 1882, Mem. 1, 45—74).—This mineral belongs to a remarkable class of crystals, which, with forms decidedly belonging to the regular system, nevertheless act on polarised light like double-refracting bodies. This anomaly in analcime, first observed by Brewster (*Phil. Trans.*, 1818, 255), has been attributed by Mallard (*Annales des Mines*, 10, 1876) to the building up of the analcime crystal by the union of parts of crystals belonging to other systems, and by Arzruni and Koch (*Zeitschr. f. Krystallographie*, 2, 1881) to the different degrees of density of the crystals in different crystallographic directions. The author of the present paper, however, regards these modes of explanation as unsatisfactory, and ascribes the double refraction of the analcime crystals to a state of internal tension. The existence of such a state of tension is in fact indicated by the presence of fissures, which are most numerous in the largest crystals; and its power of producing a double-refracting structure in originally homogeneous masses, is shown by experiments on gelatin and other colloid bodies. This effect, first observed by Brewster, in 1835, has been further demonstrated by the author by casting gelatin in moulds having the forms of the cube, octohedron, dodecahedron, and other forms of the regular system. The geometric forms of gelatin thus obtained acted on polarised light similarly to crystals of analcime, the effect arising from the tension consequent on the drying of the mass.

H. W.

**Sodalite from Tiahuanaco.** By BAMBERGER and FEUSSNER (*Zeitschr. f. Kryst.*, 1881, 580—585; *Jahrb. f. Min.*, 1882, 1, Ref., 27).—The material examined was found in isolated lumps in the ruins of Tiahuanaco, in Southern Peru, apparently derived from some unknown

locality, as sodalite has not hitherto been found native in South America; perhaps a refuse from the preparation of pearls from that mineral. The lumps are blue and crystalline, like sodalite from Ditre and Minsk, and associated with spathic iron, iron pyrites, and brown hæmatite. The indices of refraction of this mineral for the lithium, sodium, and thallium lines agree almost exactly with those of crystallised sodalite from Vesuvius. The spectroscope shows that the blue colour is due to a strong absorption of the red and yellow rays.

Chemical analysis gave the numbers I; under II are given those obtained after deduction of impurities, and calculation of the  $K_2O$  or  $Na_2O$ ; and under III, the calculation of the latter result to 100.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	Na <sub>2</sub> O.	Na.	K <sub>2</sub> O.	Cl.	H <sub>2</sub> O.
I ..	37·96	30·96	0·85	0·46	18·28	3·45	0·74	5·34	1·10 = 99·14
II ..	37·96	30·96	—	—	18·77	3·45	—	5·34	— = 96·48
III ..	39·34	32·09	—	—	19·45	3·58	—	5·54	— = 100·00
IV ..	38·19	32·77	—	—	19·73	3·66	—	5·65	— = 100·00

Hence the formula  $NaCl + 2(Al_2O_3, Na_2O, 2SiO_2)$ , which gives the numbers under IV, showing that the ratio of chloride to silicate is as 1 : 2, and not 2 : 3, as hitherto supposed for all sodalites. The substance dissolves in acids at the ordinary temperature, forming a clear solution, which after some time deposits part of the silica in the gelatinous form. Sp. gr. at 21° = 2·3405 (= 2·3372, according to Stuebel).

H. W.

**Artificial Production of Peridote in the presence of Steam at the Ordinary Atmospheric Pressure.** By ST. MEUNIER (*Compt. rend.*, 93, 737—739).—The author's method (*Compt. rend.*, 27, for the production of anhydrous silicates is to expose the metal to be silicated to the simultaneous action of steam and the vapour of silicon chloride at a red heat. He thinks this method of special interest, because it is an imitation of the conditions under which the primitive minerals, such as meteorites, are produced in nature, and which appear to be working now in the sun's photosphere. He has succeeded in synthesising enstatite, peridote, and a pulverulent mixture of the two, resembling the dust from primitive meteorites, which need only be cemented with nicked iron to make it identical with the natural rock. The artificial enstatite has even the properties of arranging itself in clusters of radiating needles, to which peculiarity in the natural substance some attribute an organic origin; the author remarks that these so-called fossils can be formed in a porcelain tube, heated to redness. The artificial peridote is crystalline; boiling hydrochloric acid attacks it, dissolving the magnesium and depositing gelatinous silica. These syntheses will make the origin of very many meteorites of the common type better understood; as, for example, aumelite, chlodnite, chassignite, &c. In these experiments the mixed vapours ought not to pass through the hot tube too quickly.

D. A. L.

**Mineral Analyses.** By F. J. WILK (*Jahrb. f. Min.*, 1882, 1, Ref., 16—18).—The analyses of the following minerals were performed in the University Laboratory at Helsingfors (see p. 287). 1. Scapolite from Stansvill, near Helsingfors, where it occurs together with red

	1.		2.		3.		4.		5.		6.		7.		8.		9.		10.	
	a.	b.			a.	b.									a.	b.	a.	b.	a.	b.
Silica .....	47.6	45.6		59.97	56.92	56.44	53.45	47.74	34.53	36.73	39.03	39.51	37.73	37.42	37.09	37.42	57.09	56.68		
Alumina .....	33.5	32.6		4.98	5.10	8.63	—	—	—	16.20	17.40	16.50	11.85	12.31	16.52	12.31	16.52	17.59		
Ferric oxide .....	—	—		—	—	—	2.80	—	32.35	10.13	38.65	38.28	5.88	4.77	—	4.77	—	—		
Manganic oxide .....	—	—		—	—	—	0.68	—	—	—	—	—	—	—	—	—	—	—		
Ferrous oxide .....	—	—		19.29	1.01	2.63	—	10.10	—	—	—	—	—	—	—	—	—	—		
Lime .....	17.2	23.4		12.44	16.68	11.82	25.05	18.73	32.26	4.00	0.94	0.65	40.10	39.01	9.03	39.01	9.03	7.65		
Magnesia .....	—	—		3.99	20.99	21.12	16.12	19.36	—	2.88	2.22	3.24	3.40	4.13	—	4.13	—	—		
Potash .....	—	—		—	—	—	—	—	—	—	—	—	—	—	—	—	—	2.11		
Loss by ignition .....	—	—		—	—	—	—	3.10	—	—	—	—	—	—	—	—	—	—		
Water .....	—	—		—	—	—	—	—	—	—	—	—	—	—	17.79	—	17.79	15.94		
	98.3	101.6		100.67	100.70	100.64	98.10	99.03	99.14	99.94	98.24	98.18	98.96	97.64	100.43	97.64	100.43	99.97		

11.		12.	
Insoluble residue .....	4.77	Insoluble residue .....	4.43
Ferric oxide and alumina ..	5.19	Lime .....	29.09
Calcium carbonate .....	44.66	Magnesia .....	19.19
Magnesium carbonate ....	45.25	Ferrous oxide .....	1.52
	99.87	Carbon dioxide .....	44.99
			99.22

labradorite in a pegmatite rock.—2. Dark green hornblende from Sillböle. Sp. gr. 3·28.—3. Dark green actinolite from the chlorite slate of Orijaervi; the alumina present is attributed to admixed chlorite. Sp. gr. 2·91.—4. Green malachite from Orijaervi.—5. Malacolite from Tavastby, in Helsing; not quite fresh.—6. Iron-black mica from Stansvik.—7. Red garnet from Orijaervi. Dodecahedrons from mica-slate: the iron is mostly present as ferrous oxide.—8. Red garnet from Kidilä; icositetrahedrons from granite.—9. Idocrase from Kimito.—10. Desmin, from the Faroe Islands.—11. Dolomite, from Ranhalaks: carbon dioxide 44·12 per cent.—12. Fine-grained marble-like dolomite from Kulkinmaa in Nieder-Torneaa; sp. gr. 2·83; mean of four analyses. H. W.

**Preliminary Notice of Substances which may prove to be New Minerals. Note on Abriachanite;** by M. FORSTER HEDDLE (*Min. Mag.*, 3, 57, 193; 4, 117 and 189).—**Note on the Occurrence and Localities of Abriachanite.** By T. AIKIN (*ibid.*, 3, 69; *Abstr., Jahrb. f. Min.*, 1882, 1, Ref., 8).—1. *Bhreckite*. This fine-grained, somewhat laminar mineral, having a soft and friable texture and light apple-green colour, was found in very small quantity, associated with iron-glance and calciferous strontianite, on brown quartz-crystals in a granite vein on the declivity of the Ben Bhreck, near Tongue, in Sutherlandshire. Analyses gave:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	Alkalis.	H <sub>2</sub> O.
34·92	7·16	12·71	2·11	0·41	16·08	8·26	traces	17·77 = 99·42

The mineral gives off 1·033 per cent. water at 100°, and dissolves easily in hydrochloric acid. It is almost the only known mineral resembling chlorite which contains a considerable amount of lime; and if its separate identity should be established, it would be related to Asp's chronicrite and metaxoite.

2. *Xantholite*.—The rough crystals, of the size of beans, surrounded by biotite, are nodular, of colophony to cinnamon colour, very much fissured, and have only one perceptible direction of cleavage. Fracture conchoidal with glassy lustre. Harder than the knife, but uncommonly brittle. Gives off 0·64 per cent. water at 100°.

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	F.	H <sub>2</sub> O.
27·04	45·86	8·67	6·90	0·56	3·81	4·32	0·09	2·88 = 100·13
27·20	45·97	8·61	6·91	0·50	3·53	4·50	undet.	2·87 = 100·09

The author is inclined to regard the mineral as a dimorphous form of "grenatite" (staurolite), especially as minute enclosed crystals, probably of the same substance, indicate monoclinic symmetry.

Xantholite occurs at Milltown, on Loch Ness, in a peculiar rock, consisting of edenite and a highly calciferous biotite resembling talc, and in company with wollastonite, hydrous anthophyllite, red granite, and zircon. The mineral from Loch Ness, supposed to be chondrodite, was probably xantholite.

3. *Abriachanite*.—In the neighbourhood of Abriachan, on the north-east shore of Loch Ness, sometimes in decomposed granite, sometimes

in perfectly fresh granite-veins, this mineral is found filling the veins and cracks which traverse the rock in all directions. It has a whitish-blue to blue colour, finely fibrous structure, and silky lustre. In contact with water, it swells up, and may be trituated with it to an argillaceous mud. This mud, freed from impurities by suspension in water, gave by analysis:—

SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	S.
52.40	9.34	15.17	0.40	1.18	10.50	0.61	7.11	2.97	1.00 = 100.68

It gives off 0.57 per cent. water at 100°. Sp. gr. = 3.326. Before the blowpipe, it gives the sodium flame and the reaction of iron, and melts with difficulty to a black tumefied strongly magnetic glass. Its powder is insoluble in all acids.

4. *Balvraidite*.—A pale purple-brown saccharogranular crystalline mineral, occurring in the granular limestone near the village of Balvraid, in Glen Elg, Inverness-shire, together with blue necronite, biotite, and the hydrated labradorite described below; H. = 6; sp. gr. = 2.905. The colour varies somewhat in depth but not in tone. Altogether the mineral is remarkably like bytownite. Before the blowpipe, it melts with tumefaction to a blistered pale-blue glass. Under the microscope it appears homogeneous. Analysis gave: *a*, dark variety; *b*, light.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MnO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.
<i>a</i> .	46.04	20.11	2.52	0.78	13.47	8.30	1.36	2.72	4.71 = 100.01
<i>b</i> .	46.17	20.95	1.86	0.84	13.25	7.36	1.56	3.25	4.90 = 100.14
	—	22.28	1.95	0.66	13.93	8.20	—	—	4.80

These numbers do not lead to any simple formula.

5. *Hydrated Labradorite*.—No peculiar efflorescence was observable, the white waxy mineral rather appearing fresh, with flat fibrous structure, rarely granular. Before the blowpipe, it frothed like a zeolite, and fused with moderate facility to a transparent blistered glass. When slowly heated, the mineral forcibly split up into laminæ before fusing. Analysis gave:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.
49.33	26.70	0.25	11.02	0.07	2.59	5.25	4.85 = 100.06

The possibility of balvraidite being a compound (perhaps formed by fusion) of labradorite and biotite, which latter is enclosed in both minerals in fresh tablets, is denied by the author.

6. *Tobermorite*.—A massive, very fine-grained zeolite, translucent, white, with rosy streak, completely filling small geodes, and most frequently surrounded with a thin bluish zone of mesolite. From the strand, north of Tobermory, Isle of Mull. Sp. gr. 2.423.

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.
46.51	2.40	1.14	1.85	33.40	0.47	1.45	0.36	12.61 = 100.19
46.62	3.90	0.66	1.08	33.98	—	0.57	0.89	12.11 = 99.81

These numbers lead to the formula  $3(4\text{CaO}, \text{H}_2\text{O}, 5\text{SiO}_2) + 10\text{H}_2\text{O}$ ; according to which the mineral stands between okenite and zona-

lite. The latter is found at several places in the Isle of Mull. Subsequently tobermorite has been found at Dunvegan, Isle of Skye, where it is surrounded by faröelite. Gyrolite has also been found in the same neighbourhood.

7. *Walkerite*.—A mineral discovered in the last century, by Dr. Walker in the diabase of the Costorphine Hill, near Edinburgh. It occurs in veins, up to an inch thick, in the form of radio-fibrous or cauline tufts, with high, almost mother-of-pearl, lustre, and reddish-white colour.  $H. = 4.5$ . Sp. gr. 2.712. Phosphoresces when broken. Analysis gave:—

SiO <sub>2</sub> .	FeO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.
52.20	1.34	28.64	5.12	0.85	6.50	5.27 = 99.92

leading to the formula  $4CaO, MgO, Na_2O, H_2O, 7SiO_2 + H_2O$ . Walkerite is therefore nearly related to pectolite.

8. *Tyreeite*.—The author endeavoured to determine the nature of the body which produces the red spots on the beautiful cornelian marble of Tyree; but the analysis did not lead to very definite results.

H. W.

**Stilbite from the Miage Glacier, Mont Blanc.** By A. COSSA *Atti della R. Accad. dei Lincei* [3], *Transunti*, 5, 86 [1881]; *Jahrb. f. Min.*, 1882, 1, Ref., 29).—Stilbite (desmin) occurs at a height of 3700 m. in a cleft in the gneiss which rises from the Miage Glacier above the Aiguille grise towards the Dôme de Gouter. It had previously been found on the morain of the same glacier, together with other minerals, by A. Favre. It is a white radio-fibrous mass containing a few but distinct crystals of heulandite. Lustre on the cleavage-faces nacreous; on the natural faces vitreous.  $H. = 3.5$ . Sp. gr. = 2.14 to 2.18 at 15°.

The mineral gives off part of its water at 100°, but recovers it on exposure to the air; at a red heat, however, it parts with all its water, and does not afterwards recover it. Hydrochloric acid decomposes it, but not very easily, with separation of pulverulent silica.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	Na <sub>2</sub> O.	H <sub>2</sub> O.
Anal. ....	56.47	17.09	7.74	trace	18.26 = 99.56
Calc. ....	57.41	16.43	8.93	—	17.23 = 100.00

H. W.

**Analysis of Thorite from Hitterö.** By G. LINDSTRÖM (*Jahrb. f. Min.*, 1882, 1, Ref., 29).—The mineral examined agreed very well, both in appearance and chemical composition, with the thorite from Arendal, analysed by Nordenskiöld.

Silica .....	17.47	Manganous oxide ....	0.43
Phosphoric oxide ....	0.93	Lime .....	1.39
Lead oxide.....	1.26	Magnesia .....	0.05
Thoria .....	48.66	Lime .....	0.18
Yttrium-earths.....	1.58	Soda .....	0.12
Cerium oxides .....	1.54	Loss by ignition.....	10.88
Ferric oxide .....	6.59		
Uranous oxide .....	9.00		100.20
Alumina .....	0.12		H. W.

**Analyses of two Minerals from Laangban.** By G. LINDSTRÖM (*Öfversigt af Kongl. Vetenskaps-Akademiens Förhandlingar*, Stockholm, 1880, No. 6, 53—58; *Jahrb. f. Min.*, 1882, 1, Ref., 30).—1. *Melanotekite*, so-called from its behaviour before the blowpipe (fusion to a black bead), and its relation to hyalotekite (Abstr., 1879, 22), is a black to blackish-grey mineral, often with a bluish tinge. Streak, greenish-grey. Lustre, metallic to fatty. Fracture, even to flat-conchoidal. Hardness 6·5. Sp. gr. 5·73 (or probably a little higher, as the mineral could not be completely freed from admixtures of magnetite and garnet). Translucent only in thin layers. Colour, bottle-green and red-brown. Cleavable in two directions with different degrees of facility. It is decomposed by nitric acid. Melts before the blowpipe, with intumescence, to a black bead; fused with sodium carbonate, it yields a button and incrustation of lead; the borax bead is red-brown in the oxidising flame while hot, yellow on cooling, dingy brown-green in the reducing flame. The saturated bead in the former case remains red-brown even after cooling; in the latter, it turns black. The phosphorus salt bead gives a skeleton of silica.

Melanotekite occurs associated with lead, often mixed with magnetite, and almost always interpenetrated by yellow garnet; the microscope shows also the presence of a pyroxenic mineral. To remove these admixtures, the purest splinters were pulverised and levigated, and the lighter portion, free from lead, was treated with the magnet. Direct analysis gave the numbers I, whilst II exhibits the composition after deduction of 2·56 per cent. garnet. III is a check analysis made upon another specimen.

	I.	II.	III.
Silica (and garnet)....	19·43	17·32	17·22
Ferric oxide.....	22·58	23·18	22·81
Lead oxide .....	53·85	55·26	58·42
Cupric oxide .....	0·20	0·20	—
Ferrous oxide .....	0·73	0·75	—
Manganous oxide.....	0·67	0·69	0·57
Lime.....	0·02	0·02	—
Magnesia .....	0·57	0·59	0·33
Potassium oxide .....	0·23	0·24	0·18
Sodium oxide .....	0·53	0·54	0·33
Baryta (?) .....	0·10	0·11	—
Chlorine .....	0·14	0·14	—
Phosphoric oxide.....	0·07	0·07	—
Loss by ignition .....	0·93	0·93	—
	100·05	100·04	—

These numbers lead to the formula  $2\text{RO}, \text{SiO}_2 + \text{Fe}_2\text{O}_3, \text{SiO}_2$ , in which  $\text{RO} = \frac{5}{6}\text{PbO} + \frac{1}{6}(\text{CuO}, \text{FeO}, \text{MnO}, \text{CaO}, \text{MgO}, \text{K}_2\text{O}, \text{Na}_2\text{O})$ . Lindström observes that if the manganese in kentrolite, lately described by Damour and vom Rath, be regarded as sesquioxide, the formula of that mineral will become  $2\text{PbO}, \text{SiO}_2 + \text{Mn}_2\text{O}_3, \text{SiO}_2$ , and will indicate isomorphism with melanotekite.

2. Lindström also gives the analysis of a bustamite from Laangban,

a mineral new for Sweden. It occurs together with schefferite; is fine-cauliform; red, reddish-grey or grey; translucent; has a strong vitreous to silky lustre; melts easily before the blowpipe, giving the reaction of manganese; and exhibits two directions of cleavage nearly at right angles to each other. Sp. gr. 3.40. Analysis gave:—

SiO <sub>2</sub> .	MnO.	FeO.	CaO.	MgO.	BaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Pp. with SH <sub>2</sub> .	
47.66	31.65	0.48	18.16	1.18	0.19	0.12	0.15	0.52	= 100.11
									H. W.

**Existence of Epidote in the Syenite of the Ravin d'Enval, near Riom (Puy-de-Dôme).** By F. GONNARD (*Bull. Soc. Min. de la France*, 1880, 3, 173; *Jahrb. f. Min.*, 1882, 1, Ref., 23).—Epidote has hitherto been found but rarely in the Department of Puy-de-Dôme. Bouillet mentions it as occurring in granules in syenite from the foot of the Puy-de-la-Rodde. Lecoq mentions its occurrence in the diorites above La Pradelle, near the village of Volvic (Riom). v. Lasaulx found it in yellowish microscopic crystals in the rock called "petrosilex céroïde," near the Puy-de-Berzet. The epidote found by the author occurs as a group of small green crystals in veins of a syenite, consisting of reddish felspar and green or black hornblende. He has also observed the occurrence of compact epidote in veins of somewhat lighter colour, resembling that from the Ravin d'Enfer in the Pyrenees.

H. W.

**Existence of a Mineral Analogous to Tachylyte in a Basalt of the Environs of Royat (Puy-de-Dôme).** By F. GONNARD (*Bull. Soc. Min. de la France*, 1880, 3, 321; *Jahrb. f. Min.*, 1882, 1, Ref., 23).—Crusts of a nut-brown to green substance, approximating in physical properties to the basic vitreous rock called tachylyte, are found in cavities of basalt, associated with groups of calcite crystals, on which are implanted transparent aragonites of the form  $\infty P. \infty P\infty. P\infty$ . This substance, however, differs from tachylyte in not being attracted by the magnet, and in not dissolving readily in hydrochloric acid. This last property indicates a transition to hyalomelane.

H. W.

**Synthesis of Meteorites.** By F. FOUQUÉ and M. LÉVY (*Compt. rend.*, 93, 674—675).—By igneous fusion the authors have succeeded in reproducing two crystalline types of minerals analogous to certain oligosidereal meteorites. The first, consisting of minerals free from felspar, are composed simply of silica, magnesia, and iron, and contain peridotite, enstatite, ferrous oxide, and magnesian pyroxene; they have a contracted form and a granitoidal structure. The ferrous oxide is sometimes in isolated crystals, and sometimes accumulates in the interstices of the other minerals; it is easily reduced to metallic iron by exposure to the action of coal-gas at a low red heat. The magnesian pyroxene is identical with Ebelmen's magnesian diopside.

The second are feldspathic, and contain anorthite associated with



pyroxene and enstatite, or with peridot. Their structure resembles that of the ophites.

The only notable difference between these artificial minerals and the natural ones is, that the latter are generally crumbly, whilst the former are very solid.

D. A. L.

**Composition of the Mineral Water of Baréges.** By E. FILHOL (*J. Pharm. Chim.* [5], 4, 546—548).—The water of the Spring Barzun, near the village of Baréges, has been carried to Luz for therapeutic purposes; and in so doing the composition of the water has undergone little or no change.

It contains chiefly sodium hydrogen sulphide, and on heating it with sulphur, a thiosulphate and a further quantity of sulphide is formed, owing to the decomposition of the sodium silicate present.

L. T. O'S.

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## Organic Chemistry.

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**Some Salts of Chromium and Mercury.** By F. W. CLARKE and D. STERN (*Am. Chem. J.*, **3**, 351—354).—The following double salts of mercuric chloride and cyanide with alkaline chromates have long been known:—

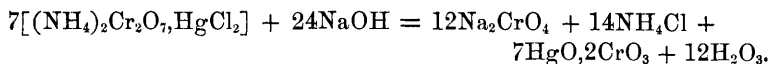
- |  |                               |
|--|-------------------------------|
| 1. $(\text{NH}_4)_2\text{Cr}_2\text{O}_7, \text{HgCl}_2, \text{H}_2\text{O}..$ | Darby, Richmond u. Abel.      |
| 2. $3(\text{NH}_4)_2\text{Cr}_2\text{O}_7, \text{HgCl}_2$ . . . .              | Richmond u. Abel.             |
| 3. $\text{K}_2\text{Cr}_2\text{O}_7, \text{HgCl}_2$ . . . . .                  | Millon, Darby.                |
| 4. $\text{K}_2\text{Cr}_2\text{O}_7, 2\text{HgCl}_2$ . . . . .                 | Darby.                        |
| 5. $\text{K}_2\text{Cr}_2\text{O}_7, 2\text{HgCy}_2$ . . . . .                 | Poggiale, Caillot u. Podevin. |
| 6. $\text{Ag}_2\text{Cr}_2\text{O}_7, 2\text{HgCy}_2$ . . . . .                | Darby.                        |

The first of these compounds (anhydrous, however, according to the authors of this paper) is deposited in large showy crystals from the concentrated solution of its two component salts in equivalent proportions. It was found to contain 19·80 per cent. chromium, the theoretical percentage for the anhydrous salt being 19·88; whereas for a monohydrated salt it would be 19·22.

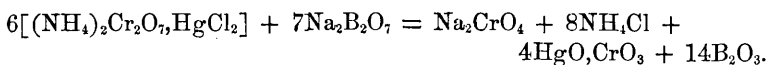
From the mother-liquor of this compound, Richmond and Abel obtained the salt numbered 2. Clarke and Stern, however, failed to obtain this salt, or indeed any definite compound, from the mother-liquor in question. On adding ammonia, a heavy dirty-yellow precipitate was at first formed, which redissolved in an excess of the precipitant, the solution depositing a small quantity of dark clove-brown granular crystals, probably consisting of an ammonium chromate combined with a chromate of one of the mercurammonium bases.

On adding a caustic alkali to a solution of the salt,  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7, \text{HgCl}_2$ , a yellow precipitate is formed, consisting of a basic chromate of mercury. From hot solutions, precipitates were obtained of variable composition, but cold solutions yielded the salt  $7\text{HgO} \cdot 2\text{CrO}_3$ , previously obtained in Professor Clarke's laboratory by Miss Helena Stallo, and

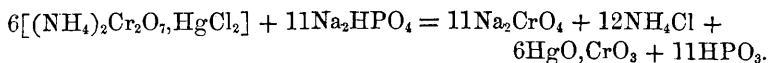
in a different way by Geuther (*Annalen*, **106**, 244). Its formation is represented by the equation:—



The addition of a solution of borax to a solution of the salt,  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7, \text{HgCl}_2$ , produces a yellow precipitate, whose composition agrees approximately with the formula  $4\text{HgO}, \text{CrO}_3$ : on concentrating the filtrate from this precipitate, it yielded white crystals of boric acid, probably formed according to the equation:—



If, instead of borax, hydrogen-disodium phosphate be used as the precipitant, another basic chromate is thrown down, viz.,  $6\text{HgO}, \text{CrO}_3$ :—



These results establish definitely the existence of the basic chromate  $7\text{HgO}, 2\text{CrO}_3$ , and render the existence of two other basic mercuric chromates highly probable.

The salts numbered 3 and 4 in the preceding list were found difficult to purify. To number 5 Darby and Rammelsberg both assign the formula  $2\text{K}_2\text{CrO}_4, 3\text{HgCy}_2$ , requiring 9.09 per cent. chromium, whereas the simpler formula,  $\text{K}_2\text{CrO}_4, 2\text{HgCy}_2$ , above given requires 7.45. The authors' experiments gave 7.62 per cent., confirming the latter formula. The salt numbered 6 was easily prepared, and its composition verified. The authors tried, but unsuccessfully, to obtain a corresponding salt containing thallium in place of silver; neither did they succeed in producing double salts of mercuric cyanide with ammonium chromate, ammonium dichromate, or potassium dichromate; or of mercuric chloride with ammonium chromate. H. W.

**Action of Hydriodic Acid on Propylene Chloriodide and Isopropyl Chloride.** By R. D. SILVA (*Compt. rend.*, **93**, 739—741).—In a former communication, the author described the action of hydriodic acid on epichlorhydrin, with the production of normal propyl chloride and a small quantity of a propyl iodide. These results led him to think that of the two probable formula for propylene chloriodide,  $\text{CHMeCl}.\text{CH}_2\text{I}$  and  $\text{CHMeI}.\text{CH}_2\text{Cl}$ , the former is the right one, an inference which is confirmed by the present experiments.

When a current of hydriodic acid gas is passed into the chloriodide heated to  $100^\circ$ , isopropyl iodide is obtained, with separation of iodine. Hydriodic acid and the chloriodide also, when mixed in molecular proportions and heated in sealed tubes in a water-bath, gave rise to isopropyl chloride (b. p. about  $36^\circ$ ).

By heating isopropyl chloride in sealed tubes with hydriodic acid on a water-bath for 14 to 20 hours, it is converted into isopropyl iodide;

in one experiment, where 40 grams were used, only 3 or 4 remained unaltered.

D. A. L.

**Action of Zinc-ethyl and Zinc-methyl on Chlorinated Aldehydes.** By K. THURNLACKH (*Annalen*, **210**, 63—79).—As Wagner (*ibid.*, **175**, 361) had obtained methylethylcarbinol by the action of zinc-ethyl on aldehyde, the author thought it advisable to extend the investigation to the chlorinated derivatives of aldehydes.

*Zinc-ethyl and Chloral*.—The chloral diluted with ether is run slowly into an ethereal solution of zinc-ethyl. The reaction takes place in the cold, with evolution of gas and formation of the crystalline compound  $\text{CCl}_3\cdot\text{CH}_2\cdot\text{OZnEt}$ , which when decomposed with water, gives zinc hydroxide, ethane, and *trichlorethyl alcohol*,  $\text{CCl}_3\cdot\text{CH}_2\cdot\text{OH}$ , which crystallises in rhombic tablets (m. p.  $17\cdot8^\circ$ , b. p.  $151^\circ$ , bar. = 737 mm., vap. dens. found  $5\cdot14$ , calc.  $5\cdot18$ ), only slightly soluble in water, but soluble in all proportions in alcohol and ether. It has a pleasant ethereal odour. Its sp. gr. =  $1\cdot5500$  at  $23\cdot3^\circ$ . Digested with acetic chloride in sealed tubes at  $120\text{--}130^\circ$ , it forms *trichlorethyl acetate*,  $\text{CCl}_3\cdot\text{CH}_2\cdot\text{OAc}$ , an aromatic colourless oily liquid (vap. dens. found  $6\cdot89$ , calc.  $6\cdot63$ , b. p., with decomposition,  $167^\circ$  at 736 mm., without decomposition,  $71^\circ$  at  $18\cdot3$  mm.), insoluble in water, and sp. gr.  $1\cdot3907$  at  $23\cdot3^\circ$ . By oxidation with strong nitric acid, in which the trichlorethyl alcohol dissolves with slight rise of temperature, *trichloroacetic acid* is formed. *Lead trichloracetate*,  $(\text{C}_2\text{Cl}_3\text{O}_2)_2\text{Pb} + \frac{1}{2}\text{H}_2\text{O}$ , is entirely decomposed by drying at  $100^\circ$ . Potash solution (sp. gr.  $1\cdot25$ ) dissolves trichlorethyl alcohol, and after a short time gives rise to a very violent reaction. If, however, the potash solution is added drop by drop to the alcohol as long as there is any oil floating on the surface the reaction is complete, and goes on quietly: the product is chiefly *trichlorethylglycollic acid*,  $\text{CCl}_3\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{COOH}$ ; it forms small rhombic leaflets (m. p.  $69\cdot5^\circ$ ), soluble in ether, alcohol, and boiling water, very slightly in cold. By repeated fusion, it seems to give off water. The salts of this acid decompose when their solutions are boiled for a long time. The *calcium salt*,  $(\text{C}_4\text{H}_4\text{Cl}_3\text{O}_3)_2\text{Ca} + 3\text{H}_2\text{O}$ , crystallises in tufts of shining needles, easily soluble in water; the  $3\text{H}_2\text{O}$  go off at  $120^\circ$ . The *silver salt*,  $\text{C}_4\text{H}_4\text{Cl}_3\text{O}_3\text{Ag}$ , separates from its aqueous solution in hemispherical aggregations of thin broad needles, which turn black very quickly in the light. Besides this acid, small quantities of monochloroacetic and formic acids are produced.

*Zinc-methyl and Chloral*.—This reaction does not go on so violently as with the zinc-ethyl. The product is a gummy mass, and is decomposed by dilute hydrochloric acid with the evolution of gas and the separation of an oil. This oil consisted chiefly of *trichloropropyl alcohol*,  $\text{CCl}_3\cdot\text{CHMe}\cdot\text{OH}$ , which crystallises in small colourless needles, easily soluble in alcohol and ether, and running to an oil when brought in contact with water. It melts at  $49\cdot2^\circ$ , sublimes at the ordinary temperature, and boils between  $150\text{--}160^\circ$  (vap. dens. found  $5\cdot48$ , calc.  $5\cdot66$ ). It has an agreeable aromatic camphor-like odour. Concentrated solutions of potash dissolve it; the solution, however, soon decomposes with the separation of oily bodies.

D. A. L.

**Preparation of Ethyl Acetate** (*Dingl. polyt. J.*, **242**, 231).—150 kilos. fused sodium acetate, 150 kilos. alcohol of 23 per cent. (Tralles), and 135 kilos. sulphuric acid, 66° B., are distilled with steam in a large copper still with jacketted bottom. The distillate was separated into three fractions, the total quantity of crude ether obtained amounting to 233 kilos. Another quality of sodium acetate gave 363 kilos. crude ether from a mixture of 250 kilos. sodium acetate, 250 kilos. alcohol, and 225 kilos. sulphuric acid. The crude product is agitated with lime, the residue separated, and the ether rectified with steam-heat. From the above 363 kilos. crude ether 334 kilos. rectified ether are obtained. To produce absolute acetic ether, the rectified product is washed with water, then treated with potash, and distilled. D. B.

**Production of Furfural by the Dry Distillation of Wood.** By H. B. HILL (*Am. Chem. J.*, **3**, 33—37).—In this paper, the author gives a brief description of the dry distillation of wood, as practised at Brooklyn, New York, for the manufacture of acetic acid. The wood, chiefly oak, is cut into small pieces and filled into rectangular retorts of boiler iron, each capable of containing a charge of five to six thousand kilograms, and placed in separate cells of an oven heated by hot-air flues, the temperature being carefully regulated by thermometers built into each cell, from 150° at the beginning to 200° at the end of the distillation. The volatile products of the distillation are rectified in the usual way. In fractioning the crude wood-spirit, the distillate obtained after the more volatile portions have passed over, yields on dilution with water, a heavy yellow oil; and somewhat later the slightly acid aqueous distillate contains an abundance of the same oil in suspension, the total quantity obtained amounting to between 0·3 and 0·4 per cent. of the crude wood-spirit taken.

This oil, after being washed with water, dried over calcium chloride, and repeatedly rectified, distilled between 162° and 165°, the greater part boiling steadily at 162°. The boiling point and general character of the oil at once suggested the presence of furfural, and this was easily proved by its conversion into furfuramide, furfurine, and pyromucic acid. Its behaviour with alkalis, however, showed that it was not quite homogeneous, for when shaken with dilute potash or soda-ley, it assumed a brilliant yellow colour, and in a few moments became turbid from separation of a flocculent yellow precipitate, which proved to be chiefly pyroxanthin (p. 306).

The production of furfural by the dry distillation of wood appears to have been first noticed, although by no means satisfactorily established, by Völkel (*Annalen*, **86**, 65). V. Meyer afterwards found a small quantity of it in glacial acetic acid (*Ber.*, **11**, 1870). Greville Williams (*Chem. News*, **26**, 231, 293) found that it was formed when wood was heated with water under pressure, although none could be obtained at ordinary pressures; and similar results were obtained by H. Müller (*ibid.*, **247**). H. W.

**Constitution of the Thiohydantoïns and Thiocarbamates.** By C. LIEBERMANN (*Annalen*, **207**, 121—167).—Diphenylthiohydan-

toin prepared by Lange (*Ber.*, **12**, 595) was found to split up on treatment with dilute alkali into diphenylcarbamide and thioglycollic acid; this decomposition was not altogether unexpected, inasmuch as Jäger's phenylcarbodiimidothioacetic acid, prepared in a way by which phenylthiocarbamide can also be obtained, likewise yields thioglycollic acid to potash. According to the accepted formula of thiohydantoïn,

$\text{CS} \begin{array}{c} \text{NH.CH}_2 \\ | \\ \text{NH.CO} \end{array}$ , it does not appear how thioglycollic acid can be formed

by its decomposition; it seemed therefore of interest to investigate the cause of this apparent discrepancy, and experiments with this object were made in common with A. Lange. Thioglycollic acid was obtained in quantity from diphenylthiohydantoïn, and carefully examined, and its barium, lead, and mercury salts prepared and analysed: the lead salt proved to be normal, and not basic like that described by Claesson.

From diphenylthiohydantoïn, a body having the formula  $\text{C}_9\text{H}_7\text{NSO}_2$  can be obtained by heating it with hydrochloric acid. On experiment this was also found to yield thioglycollic acid by heating with an alkali.

That the thioglycollic acid formed in these decompositions was not the result of a secondary action was proved by direct experiment; glycollic acid was digested with alkaline sulphides and with diphenylthiocarbamide, but no thioglycollic acid was produced.

In order therefore to account for this formation of thioglycollic acid, thiohydantoïn must be formulated thus:  $\text{NH}:\text{C} \begin{array}{c} \text{S.CH}_2 \\ \text{---NH---} \end{array} \text{CO}$ , and thiohydantoic acid,  $\text{NH}:\text{C}(\text{NH}_2).\text{S.CH}_2.\text{COOH}$ . Obviously, therefore, monosubstitution derivatives must exist in two forms, according to the atom of nitrogen to which they are attached. Jäger's phenylcarbodiimidoacetic acid would then be really one of the monophenylthiohydantoic acids, and P. Meyer's phenylthiohydantoïn one of the substituted thiohydantoïns, the substitution having probably been different in each case, as they are not convertible one into the other. In like manner, the body  $\text{C}_9\text{H}_7\text{NSO}_2$  can be shown to have two possible isomeric forms, like its analogue thiocarbamacetic acid formed by the decomposition of thiohydantoïn with an acid.

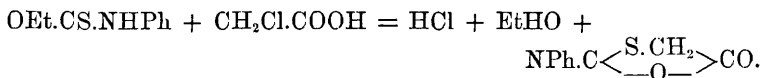
In order to bring the new formula for thiohydantoïn into accord with its synthesis from thiocarbamide and chloracetic acid, we must first assume the formation of an addition-product—



by which the double linking of sulphur to carbon is loosed, hydrochloric acid being afterwards set free, and thiohydantoic acid formed. A case analogous to this is furnished in the formation of the bromide of ethylthiacetanilide from thiacetanilid and ethyl bromide (Wallach and Bleibtren, *Ber.*, **12**, 1061). Here also the ethyl enters into combination with a sulphur-atom previously linked by both its affinities to carbon: numerous other instances are also cited by the same authors. In the formation of chlorphenylthiocarbimide Hofmann has also been obliged to make a similar assumption.

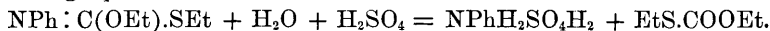
Thiocarbamide also combines directly with ethyl iodide or bromide, forming compounds which on decomposition yield thiocyanates and mercaptan, whereas thiohydantoin in such circumstances is inactive, the reason of this probably being that it no longer contains the group C:S. The absence of this group also explains the fact noticed before by several observers, that the thiocarbamides yield up their sulphur much more readily than the thiohydantoins. And lastly, as a reason for accepting the new formula, Andreasch has recently built up thiohydantoin from cyanamide and thioglycollic acid.

The body,  $C_9H_7NO_2S$ , above alluded to may be prepared by heating in a sealed tube a mixture of phenyl thiocarbamate and chloracetic acid—



To this substance the author gives the name of phenyl thiocarbimid-glycolide: it can also be prepared directly from phenyl thiocarbimide and chloracetic acid: here also, therefore, we have the breaking up of the group CS.

The question next arose, as to whether this breaking up of the group CS occurred in the formation of other addition-products of the thiocarbimides, and particularly in the case of the thiocarbamates. The latter form salts with alkalis, from which they are precipitated by acids, and may thus be purified. Phenyl thiocarbamate treated this way was found to melt at  $71^\circ$ . The potassium and sodium compounds are not easily prepared, but the silver derivative was easily formed by precipitation with an ammoniacal solution of the silver oxide. Methyl phenylthiocarbamate is obtained by warming a mixture of methyl iodide and the silver salt suspended in ether: it boils at  $260\text{--}265^\circ$  with slight decomposition. The ethyl salt (m. p.  $30^\circ$ , b. p.  $278\text{--}280^\circ$ ) is obtained in a similar way; they are both insoluble in water and alkalis. An easier method of preparation is to heat the alkaline solution of phenyl thiocarbamate with alcoholic iodides until the alkaline reaction has disappeared; if too much alkali has been used, mercaptan is also produced. It appears that the etheric salts cannot be prepared without the direct intervention of alkalis—a fact which does not harmonise with the acceptance of the formula  $EtO.CS.NHPh$  for ethylic phenylthiocarbamate; neither does it agree with the formation of silver and alkaline salts. The ethyl salt should also yield ethylaniline on decomposition. It was therefore heated for some time with dilute sulphuric acid: a strong odour of mercaptan was observed, and a strongly refractive oil distilled over which, on further purification, was found to boil at  $156\text{--}159^\circ$ , and showed the reactions and composition of ethyl thiocarbonate. The salt of a base was also left behind, which proved on examination to be aniline. The true formula for ethylic phenylthiocarbamate appears, therefore, in the following equation:—



According to the generally accepted formula it ought to yield ethyl-

aniline and sulphuretted hydrogen on decomposition. The methyl salt was found to behave in a manner similarly to the ethyl salt. Phenyl thiocarbamate, under the same conditions, yielded aniline, carbonic anhydride, and sulphuretted hydrogen. The methyl salt heated with aniline was decomposed into mercaptan and diphenylcarbamide: with hydrochloric acid, methyl chloride and phenyl thiocarbamate are formed.

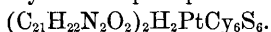
A dithio-compound can be obtained from the silver salt of phenyl thiocarbamate by treating it with iodine, just as a dithio-compound can be prepared from mercaptan: it forms fine prismatic crystals, melting at  $102^{\circ}$ , and appears to be expressed by the formula  $\text{NPh}:\text{C}(\text{OEt})\text{S}:\text{S}(\text{OEt})\text{C}:\text{NPh}$ . Paratolyl thiocarbamate, prepared by heating a mixture of paratolylthiocarbimide with absolute alcohol at  $130^{\circ}$ , is obtained in fine crystals belonging to the asymmetrical system (m. p.  $87^{\circ}$ ). The ortho-compound is a liquid, and the meta-compound forms crystals (m. p.  $67^{\circ}$ ) very like the para-derivative. They are all soluble in alkalis, and form silver salts by precipitation. The methyl and ethyl salts, prepared as in the case of phenyl thiocarbamate, boil above  $250^{\circ}$ , with slight decomposition. Their decomposition-products have been studied in detail in the case of the para-compound, and qualitatively with the others: in all cases ethyl thiocarbonate and the corresponding toluidine were detected. Whether these decomposition-products of the thiocarbamates are due to an atomic rearrangement during the process, or whether a change of formula is necessary for all the addition-products obtained from thiocarbimides, are questions which must be left for further investigation.

J. K. C.

**Some New Compounds of Platinum.** By F. W. CLARKE and MARY E. OWENS (*Am. Chem. J.*, **3**, 350).—When cold alcoholic solutions of platinic chloride and potassium cyanate are mixed, a pale buff-yellow precipitate is thrown down, which decomposes partially on heating the mixture, apparently with separation of metallic platinum, but may be obtained in a stable condition by filtration, washing with alcohol, and drying at the ordinary temperature over sulphuric acid. It is soluble in water, but quite insoluble in alcohol, and its aqueous solution is decomposed by boiling. The analysis gave numbers agreeing with the formula  $\text{K}_2\text{PtCl}_6(\text{CNO}) + \text{H}_2\text{O}$ .

Platosodiummonium chloroplatinate,  $\text{N}_4\text{H}_{12}\text{PtCl}_2, \text{PtCl}_2$  (green salt of Magnus), dissolves readily in a hot aqueous solution of potassium cyanate, yielding a dark-brown solution which, when concentrated over the water-bath, deposits pale-yellow needles, the mother-liquor yielding fine clusters of brown needles. The yellow salt contained platinum (43.93 per cent.), potassium, ammonia, water, and carbon; the brown crystals contained ammonia, platinum, and chlorine.

Strychnine chloroplatinate boiled for a short time with aqueous potassium thiocyanate, forms a blood-red solution which, on cooling, deposits a brilliant red crystalline precipitate consisting of—



H. W.

**Meta-isocymene.** By W. KELBE (*Annalen*, **210**, 1—62).—The paper mainly consists of a republication of results already published



in the *Berichte* (**13**, 388, 1157—1163, 1399—1432, 1829—1831; **14**, 1240—1241), and abstracted in this Journal (**38**, 678, 877, 878; **40**, 809). To these are now added the following details and remarks:—

*Metaisocymene* boils at 174—176°, and does not solidify at -25°; its refractive index is 1.493.

*Metaisocymenesulphonic Acids*.—Of these acids, there are four possible isomerides, and the author has observed four different forms of crystallisation in the lead salts, but has as yet only thoroughly examined two of these acids, of which the barium salts, &c., have already been described (Abstr., 1880, 878). The  $\alpha$ -acid is best prepared by recrystallising and decomposing its lead salt. On evaporating the solution, it is left as a syrup which crystallises on standing over sulphuric acid in a vacuum. It is hygroscopic, and melts at 88—90°. The barium salt is obtained crystalline by adding barium chloride to a boiling solution of the calcium salt. The *lead salt*,  $(C_{10}H_{13}SO_3)_2Pb + H_2O$ , crystallises in large glistening leaflets, only slightly soluble in water, easily in 75 per cent. alcohol. The *potassium salt*,  $C_{10}H_{13}SO_3K + 3H_2O$ , is easily soluble in water, and crystallises from its hot saturated solution in large shining tablets. The *sodium salt*,  $C_{10}H_{13}SO_3Na + H_2O$ , is very similar to the potassium salt. The *copper salt*,  $(C_{10}H_{12}SO_3)_2Cu + 2H_2O$ , forms brilliant pale-blue leaflets, very soluble in water. The *sulphamide* (*loc. cit.*) is best purified by recrystallisation from light petroleum. On treating the aqueous solution of the  $\alpha$ -acid with bromine in the cold, the bromine quickly disappears, and bromocymene is precipitated. As soon as the formation of bromocymene is once finished, the solution can be boiled with excess of bromine without any more bromocymene being produced; but if, on the other hand, the solution is heated to boiling from the beginning, the products are only bromocymene and sulphuric acid. The solution poured off from the bromocymene produced in the cold, when neutralised with lead carbonate, filtered, evaporated to dryness, and extracted with absolute alcohol, contains the lead salt of the brominated sulphonic acid; this is evaporated to dryness, the salt dissolved in water, and decomposed. *Monobrom- $\alpha$ -metaisocymenesulphonic acid* forms a syrup which turns brown when the heating is continued, and on cooling sets to a crystalline hygroscopic mass. The acid can be obtained from its solution in strong hydrochloric acid in large colourless leaflets with a mother-of-pearl-like lustre (m. p. 108—109°). It is very hygroscopic. The *lead salt*,  $(C_{10}H_{12}BrSO_3)_2Pb + 3H_2O$ , is scarcely soluble in cold water, easily in absolute alcohol, hot water, and 70 per cent. alcohol, which is the best solvent. It crystallises in tufts of needles, and loses its water at 110°.  $\alpha$ -*Metaisocymenol*,  $C_3H_7.C_6H_3Me.OH$ , is prepared in the usual way by fusing the potassium salt of the sulphonic acid with potash. It is a colourless, strongly refractive (index = 1.525) liquid (b. p. 231°), does not solidify at -25°, is moderately soluble in water, and miscible with alcohol and ether. Its odour is like that of thymol, whilst its vapour is irritating, and causes coughing. It gives but a slight violet coloration with ferric chloride. *Benzoyl- $\alpha$ -metaisocymenol* is made by digesting the  $\alpha$ -cymenol with benzoic chloride. The product crystallises from light petroleum in large monoclinic crystals\*

\* Measured by Knop and by Cathrein.

(m. p. 73°). Benzoyl- $\alpha$ -cymenol dissolves in warm nitric acid with the production of tarry products. If, however, it is first dissolved in glacial acetic acid, and then the calculated quantity of strong nitric acid added, a crystalline nitro-derivative will be formed.

*$\beta$ -Metaisocymenesulphonic acid*, prepared by decomposing the barium salt with a sufficient quantity of sulphuric acid, is a hygroscopic syrup soluble in water, alcohol, and ether. Its salts are very soluble. The barium salt and sulphamide have been already described (*loc. cit.*). The latter becomes transparent at 106°, and melts at 108°. When bromine is added to cymene in the cold, a dibromo-derivative is formed which, on treatment with alcoholic potash, is reduced and gives monobromocymene; the latter acts on silver acetate producing silver bromide. Bromine, under other circumstances, acts very energetically, and yields products which are very easily decomposed.

The author considers the formation of bromocymene from the cymenesulphonic acid mentioned above, as a reaction analogous to the oxidation of sulphurous to sulphuric acid by means of bromine and water, the only difference being that one hydrogen-atom in the acid is replaced by a hydrocarbon group. This decomposition of sulphonic acids by bromine takes place more easily when the hydrocarbon group itself is easily acted on by bromine. He then goes on to show, that if the bromine replaces the sulphonic group it will occupy the same position; but if, on the other hand, it does not replace this group, but, instead, forms a bromo-derivative of the sulphonic acid, then it will not occupy the same position as the sulphonic group. By passing chlorine, diluted with its own volume of carbonic anhydride, into the vapour of boiling cymene until the temperature is about 230°, chlorinated bodies are obtained which distil with slight decomposition. The fraction boiling below 230° gives up the greater part of its chlorine to alcoholic potash. The product, a mobile liquid, has 13.19 per cent. chlorine, and takes up bromine without the evolution of hydrobromic acid. Fraction 230—250° gives numbers for dichlorocymene, although it is most probably a mixture. Dilute nitric acid converts this chloro-derivative into metatoluic acid. Heated at 150° with alcoholic ammonia, it yields a body which is soluble in hydrochloric acid and gives a yellow precipitate with platinic chloride. *Trinitrometaisocymene*,  $C_{10}H_9(NO_2)_3$ , can be prepared by treating metaisocymene with a mixture of 1 part of fuming nitric acid and 4 parts sulphuric acid; at first the action is violent, and the mixture must be cooled; but finally, to complete the reaction, it is necessary to heat on a water-bath. It crystallises from petroleum in brilliant yellowish-white leaflets (m. p. 72—73°), very soluble in alcohol and ether. It has a characteristic musky odour. Oxidised with dilute nitric acid or chromyl chloride, metaisocymene yields metatoluic acid (compare Paternò and Scichilone, *Abstr.*, 1881, 423). The author thinks that Étard has made a slight mistake as regards the chocolate-brown powder,  $C_{10}H_{14}.2CrO_2Cl_2$  (*Ber.*, 14, 848), breaking up, on addition of water, into an aldehyde, chromic dichloride, and chromic acid; for he at least found no chromic acid present, and further suggests the improbability of an aldehyde existing in presence of chromic acid.

D. A. L.

**Orthoanisidine and Amidodimethylquinol.** By O. MÜHL-HÄUSER (*Annalen*, **207**, 235—256).—The main object of this research was to obtain the [1:2:4] trihydroxybenzene by the oxidation of orthoanisidine and removal of the methyl group. This attempt was unsuccessful, and the author confines himself chiefly to the description of orthoanisidine and its derivatives. Orthoanisidine was obtained by heating a mixture of orthonitrophenol, potash, and methyl iodide, dissolved in wood spirit, for six hours on a water-bath, and reducing the orthonitroanisoid thus produced by tin and hydrochloric acid. Orthoanisidine boils at  $226.5^{\circ}$ , and gives a wine-red colour with sulphuric acid and potassium dichromate.

Orthoanisidine hydrochloride,  $C_6H_4(OMe).NH_2.HCl$ , is formed by treating anisidine with concentrated hydrochloric acid; it forms colourless needles, soluble in water and alcohol. The hydrobromide is similar in its properties. The hydriodide crystallises in fine long needles. The nitrate and acid sulphate were obtained in colourless crystals, whilst the sulphate and oxalate are slightly tinged with red, and the picrate forms fine yellow needles.

*Acetylaniside*,  $C_6H_4(OMe).NHAc$ , obtained by heating anisidine with acetic anhydride, melts at  $78^{\circ}$ , and boils at  $302-305^{\circ}$ . Nitroacetylaniside melts at  $143^{\circ}$ , and the dinitro-compound at  $157^{\circ}$ ; they are separated by cold alcohol, in which the latter is nearly insoluble.

*Benzoylaniside*, prepared in the usual manner, forms slightly coloured crystals (m. p.  $59.5^{\circ}$ ), soluble in alcohol and ether.

*Monoanisylcarbamide*,  $C_6H_4(OMe).NH.CONH_2$ , prepared in the same way as monophenylcarbamide, forms colourless crystals (m. p.  $146.5^{\circ}$ ), soluble in hot water and alcohol.

*Dianisylcarbamide* is formed by passing carbonic oxychloride through a solution of anisidine in benzene; it is separated from anisidine hydrochloride, and purified by repeated crystallisation from alcohol. The crystals melt at  $174^{\circ}$ . Monoanisylthiocarbamide and dianisylthiocarbamide form white needles, melting at  $152^{\circ}$  and  $134.5^{\circ}$  respectively.

*Monomethylanisidine* was obtained by mixing cooled anisidine and methyl iodide together, and gradually warming the mixture. The final product was not quite pure; it boiled at  $218-220^{\circ}$ , formed salts with acids, and a platinochloride. *Dimethylanisidine*, formed by further heating with methyl iodide, is a colourless liquid, smelling like dimethylaniline. It boils at  $210-212^{\circ}$ , and has a normal vapour-density; its platinochloride is almost insoluble in water.

*Trimethylanisylammonium iodide* was formed in the preparation of the dimethyl compound in brilliant plates. By the oxidation of orthoanisidine, a methoxyquinone,  $C_6H_3(OMe)O_2$ , was formed in yellow needles (m. p.  $138^{\circ}$ ), but in such small quantities as to prevent a further investigation of its derivatives. The author therefore endeavoured to arrive at the same result from dimethylquinol, which he prepared by heating quinol with potash and methyl iodide. It was then converted into nitrodimethylquinol by dissolving it in glacial acetic acid, and treating it with dilute nitric acid. The product reduced with tin and hydrochloric acid yields the hydrochloride of amidodimethylquinol, from which the base is obtained in greenish

crystals (m. p.  $81^{\circ}$ ). All attempts, however, to prepare a hydroxy-dimethylquinol from this body were unsuccessful. J. K. C.

**Salicin.** By R. H. PARKER (*Pharm. J. Trans.* [3], 12, 378).—Various discordant numbers being given for the solubility of salicin, the author determined it carefully, and states that it may be taken as 1 in 28 for cold solution, 1 in 24 if previously dissolved by heat. The presence of glycerol slightly diminishes the solubility.

Salicin, when heated to  $268^{\circ}$ , either *per se* or dissolved in glycerol, is decomposed, yielding a brown resin, water, salicylol, and other bodies.

F. L. T.

**Paracholesterin from *Æthaliium Septicum*.** By J. REINKE and H. RODEWALD (*Annalen*, 207, 229—235).—From the dried alcoholic extract of the protoplasma of *Æthaliium septicum*, ether separates a brown oil, which solidifies on standing, and may be purified by recrystallisation from ether. This substance in its general properties shows a strong resemblance to cholesterin and ischolesterin, and more particularly to Beneke's phytosterin. It is easily soluble in chloroform and ether, and in hot alcohol. The chloroform solution, when shaken with concentrated sulphuric acid, is at first coloured yellowish-brown, but afterwards changes to blue and violet, while the sulphuric acid is gradually coloured brown, with an increasing green fluorescence. This reaction distinguishes it from normal cholesterin. Paracholesterin melts at  $134$ — $134.5^{\circ}$ , has a specific rotatory power of  $-28^{\circ}$ , and on analysis shows the same chemical composition as cholesterin. Its benzoyl-compound crystallises in thin tables with rectangular faces, and melts at  $127$ — $128^{\circ}$ ; in this respect it differs from ischolesterin. It shows great resemblance to phytosterin in everything but its specific rotatory power, which is rather lower than that of phytosterin.

J. K. C.

**Alkyl-substituted Amido-acids.** By H. SCHIFF (*Annalen*, 210, 114—123).—If the glucose only is removed from helicin, the residue consists of a crystalline body, which, on warming with hydrochloric acid, breaks up into salicylic anhydride and the hydrochloride of the amido-acid. Compounds of similar constitution can be easily formed by the direct combination of aldehydes with amido-acids, water being eliminated. In this paper some such derivatives of amidobenzoic acid, &c., are described.

By adding a warm aqueous solution of salicylaldehyde to a 5—8 per cent. solution of [1 : 3] amidobenzoic acid, [1 : 2] *hydroxybenzyleneamidobenzoic acid*,  $\text{OH.C}_6\text{H}_4.\text{CH:N.BzO}$ , crystallises out in yellow needles (melting at  $190^{\circ}$  to an orange-coloured fluid). It (the under-mentioned bodies also) is very soluble in alcohol and benzene; but is partially dissociated by warm water. Salicylaldehyde forms a similar body with [1 : 2 : 5] amidosalicylic acid. An aqueous solution of the hydrochloride of the amido-acid is mixed with the aldehyde dissolved in soda, at  $50^{\circ}$ . The body,  $\text{COOH.C}_6\text{H}_3(\text{OH}).\text{N:CH.C}_6\text{H}_4.\text{OH}$ , crystallises in colourless needles (m. p.  $245^{\circ}$  with decomposition), which turn chrome-yellow when dried in the air. By mixing aqueous solution of amidobenzoic and acetaldehyde, *ethylideneamidobenzoic acid*,  $\text{CHMe:N.BzO}$ , separates out as a white curdy mass, soon turning red.

It melts under boiling water, and by continuing the boiling gives off carbonic anhydride, and is gradually converted into a vivid red solid mass (m. p.  $200^{\circ}$ ), soluble in alcohol, which consists partially of salts of ethylidene-amidobenzoic acid and ethylideneaniline,  $\text{NPh}:\text{CHMe}$ . *Isobutyleneamidobenzoic acid*,  $\text{CHMe}_2\text{CH}:\text{N}\bar{\text{BzO}}$ , prepared from dilute solutions, crystallises in white slender needles, soluble in dilute alkalis in the cold, without decomposition. When heated, it becomes red, softens at  $130^{\circ}$ , melts about  $145\text{--}150^{\circ}$ , and decomposes completely at  $190^{\circ}$ . The ammonium salt loses half its ammonia over sulphuric acid; the solution of this salt precipitates barium and magnesium salts white; copper, pale green; nickel, flesh-coloured; ferric salts in brown flocks; silver salts on slightly warming white, but on stronger heating reduction sets in.

*Isoamylidene-amidobenzoic acid*,  $\text{CHMe}_2\text{CH}_2\text{CH}:\text{N}\bar{\text{BzO}}$ , forms white crystalline flocks, softening at  $100^{\circ}$ , melting at  $130^{\circ}$ , and decomposing above this temperature, giving off carbonic anhydride, and yielding the liquid modification of amylideneaniline. *Cinnamaldehyde* and amidobenzoic acid do not combine so readily, for even after heating at  $120^{\circ}$  for some time, only part of the mixture is converted into cinnamamidobenzoic acid, a viscous oil. The product from benzaldehyde and amidobenzoic acid could not be obtained pure. On digesting the mixed alcoholic solutions of equal weights of isatin and amidobenzoic acid with a reflux condenser, isatamidobenzoic acid,  $\text{NH}<\text{C}_6\text{H}_4>\text{C}:\text{N}\bar{\text{BzO}}$ , crystallises out in a short time, on cooling in hard yellow crystals (m. p.  $251\text{--}253^{\circ}$ ), scarcely soluble in water, with decomposition, yielding phenylimidoisatin. The compounds from the aldehydes of the fatty acids give an intense red-violet coloration (which immediately disappears) with concentrated nitric acid which has been coloured yellow with potassium dichromate. Chloral gives with amidobenzoic acid a crystalline substance, soluble in spirits of wine and in water. The behaviour of amidocuminic acid with aldehydes is similar to that of amidobenzoic acid, but the products are more stable; whilst amidoacetic acid, amido-caproic acid, tyrosine, and asparagine do not give derivatives with aldehydes without the intervention of dehydrating agents. Acetone does not act directly on amidobenzoic acid.

D. A. L.

**Aldehydosulphites of Amido-acids and Amines.** By H. SCHIFF (*Annalen*, **210**, 123—132).—The unstable sulphites of the amines and amido-acids are capable of forming stable neutral bodies with aldehydes. If aqueous solutions of amido-acids, saturated with sulphurous acid, are shaken up with aldehydes, the latter are quickly taken up with evolution of heat, and formation of very soluble compounds; these solutions on evaporation leave colourless syrups, which set slowly to white crystalline masses. With acids and alkalis these bodies behave like the aldehydesulphites. Some of them lose sulphurous acid in the desiccator. *Benzaldehydeamidobenzoic sulphite*,  $\text{COOH.C}_6\text{H}_4\text{.NH}_2 + \text{H}_2\text{SO}_3 + \text{C}_6\text{H}_5\text{.CHO}$ , partially separates out in crystals from a concentrated solution. *Cinnamamidobenzoic sulphite* is a similar body. *Cinnamidoacetic sulphite*,  $\text{C}_7\text{H}_{14}\text{O} + \text{H}_2\text{SO}_3 + \text{NH}_2\text{C}_2\text{O}_2\text{H}_3$ , is soluble in alcohol, and insoluble in ether. *Benzaldehyde-amidoacetic sulphite*,  $\text{C}_2\text{H}_5\text{NO}_2 + \text{H}_2\text{SO}_3 + \text{C}_7\text{H}_6\text{O}$ , concentrated solu-

tions set to crystalline masses. *Glycosalicylamidoacetic sulphite* was not analysed. *Glycosalicylsodium sulphite*,  $(C_6H_{11}O_4 \cdot O \cdot C_6H_4 \cdot CHO)_3NaHSO_3$ , forms white crystalline hygroscopic masses. *Isatinamidoacetic sulphite* can only be crystallised from its concentrated aqueous solution, and is very hygroscopic. *Enanthamidocaproic sulphite* could not be crystallised. *Glycosalicylamidocaproic sulphite* crystallises with great difficulty. These compounds cannot be recrystallised without decomposing.

In conjunction with A. Piutti, the author has analysed some analogous compounds which were prepared some years ago, and has hence furnished some data as regards their stability. There are some theoretical considerations. D. A. L.

**Constitution of the Arsonium and Phosphonium Compounds.** By A. MICHAELIS and A. LINK (*Annalen*, 207, 193—219).—Following the same line of thought as v. Meyer in the ammonium compounds, the authors have prepared diphenylmethyl- and diphenylethyl-arsines and phosphines, and combined them alternately with ethyl and methyl iodide, the resulting arsonium and phosphonium compounds being minutely compared in order to ascertain their divergence or identity. They have proved that the diphenylethyl-methylarsonium salts are identical in every respect with those of diphenyl-methylethyl-arsonium, and found that the same law holds good for the phosphonium compounds, thus establishing the quinivalence of phosphorus and arsenic in these combinations.

Starting from diphenylchlorarsine, prepared by dropping mercury diphenyl into excess of hot phenyldichlorarsine and heating the mixture, the chlorine was replaced by ethyl and the diphenylethylarsine (b. p.  $320^\circ$ ) thus formed combined with methyl iodide in the cold. Diphenylethylmethyl-arsonium iodide after being purified by crystallisation from a weak alkaline solution, forms white needles (m. p.  $170^\circ$ ), belonging to the rhombic system; it is almost insoluble in cold, but easily in hot water. When heated, it is decomposed into diphenylmethyl-arsine and ethyl iodide.

*Diphenylethylmethyl-arsonium Platinochloride.*—The corresponding arsonium iodide is decomposed by moist silver oxide, an aqueous solution of the hydroxide being obtained, which exhibits the usual characteristics of arsonium hydroxides, and yields a platinochloride, soluble in boiling water, and melting at  $214^\circ$  with slight decomposition.

The picrate is soluble in hot water, and crystallises therefrom in yellow needles (m. p.  $95^\circ$ ). Diphenylmethyl-arsine, prepared like ethyl-arsine, boils at  $306^\circ$ , and combines with ethyl iodide to form diphenylmethylethyl-arsonium iodide, which exhibits identically the same properties as the iodide obtained from diphenylethyl-arsine: it crystallises in the rhombic system, showing the same faces and angles, has the same solubility in water, and decomposes on heating into the same products (m. p.  $170^\circ$ ). The platinochloride and picrate are also identical with those of diphenylethylmethyl-arsonium. In a similar manner were prepared phenyldimethyl-arsonium iodide in white crystals (m. p.  $109^\circ$ ), and the corresponding platinochloride (m. p.  $219^\circ$ ). Monophenyldimethyl-arsine (b. p.  $200^\circ$ ), prepared by the action of zinc methyl on phenyldichlorarsine, forms a crystalline

iodide with methyl iodide (m. p.  $244^{\circ}$ ): the corresponding platinochloride melts at  $219^{\circ}$ .

*Diphenylchlorophosphine* was prepared by heating phosphenyl chloride with mercury diphenyl: it is a colourless oily liquid, sp. gr. 1.229 at  $15^{\circ}$ ; b. p.  $320^{\circ}$ . It oxidises easily in moist air to diphenylphosphinic acid. By treating it with zinc-methyl, diphenylmethylphosphine is obtained as a colourless, oily, strongly smelling liquid (b. p.  $284^{\circ}$ ), which absorbs oxygen rapidly. It combines easily with methyl iodide, forming diphenyldimethyl-phosphonium iodide in needles (m. p.  $241^{\circ}$ ). The corresponding platinochloride melts at  $218^{\circ}$ .

*Diphenylmethyl-phosphonium iodide* prepared from the above phosphine crystallises in the rhombic system (m. p.  $181^{\circ}$ ): the corresponding hydroxide, chloride, and platinochloride were also prepared, the latter melting at  $220^{\circ}$ . The picrate melts at  $86^{\circ}$ .

*Diphenylethylphosphine* (b. p.  $293^{\circ}$ ), obtained like the methyl compound, exhibits similar properties. From ethyl iodide the diphenyldiethylphosphonium compounds are obtained, possessing the usual characteristics; the iodide melts at  $204^{\circ}$ , and the platinochloride at  $218^{\circ}$ . With methyl iodide, diphenylethylmethyl-phosphonium iodide is formed in crystals belonging to the rhombic system, melting at  $181^{\circ}$ , and in its other properties and those of its derivatives, showing a complete identity with those of the diphenylmethylethyl-phosphonium salts. Hence it is clear that when the same number of the same organic radicals are present, the properties of the arsonium and phosphonium compounds are independent of the position of the radicals in the group. It is then in the highest degree probable that the elements of the nitrogen group are pentavalent in these compounds.

J. K. C.

**Pyroxanthin.** By H. B. HILL (*Am. Chem. J.*, **3**, 332—339).—This substance, discovered by Scanlan (1835) in the residue obtained in preparing methyl alcohol from crude wood-spirit by means of lime, was further studied in 1836 by Apjohn and Gregory (*Annalen*, **21**, 143), who deduced from their analyses the formula  $C_{21}H_{18}O_4$ . Gmelin (*Handbook*, Engl. Ed., **7**, 157) suggested the formula  $C_{10}H_8O$ , but did not support it by any experimental evidence. The author of the present paper has obtained two well-defined bromine-derivatives, from whose composition he deduces for pyroxanthin the formula  $C_{15}H_{12}O_3$ .

Pyroxanthin is the chief constituent of the yellow flocculent precipitate formed by the action of alkalis on the crude furfural obtained in the dry distillation of wood (p. 296). After the portion of this crude furfural which volatilises with steam has been distilled off, there remains a red viscous oil which partly solidifies on cooling; and on treating the semi-solid mass with small quantities of cold alcohol, the red oil dissolves, while the greater part of the pyroxanthin is left behind in minute crystals. These, having been well washed with cold alcohol, are crystallised from boiling alcohol, best with addition of bone-black, till the substance has a clear bright orange-yellow colour.

Pyroxanthin is quite insoluble in water, and very sparingly soluble in ether and in carbon sulphide; in hot alcohol, benzene or glacial acetic acid, it dissolves abundantly, and crystallises in well-developed forms on cooling. From alcohol, it crystallises in small brilliant

orange-yellow needles with blue reflex; from benzene in rather large reddish-yellow monoclinic prisms; from glacial acetic acid in flat radiate needles formed by the development of the prism in the direction of the orthodiagonal,  $a : b : c = 2.748 : 1 : 1.413$ . Angle  $ac = 87^\circ 56'$ . Observed faces,  $\infty P$ ,  $\infty P\bar{\infty}$ ,  $+ P\bar{\infty}$ ,  $- P\infty$ ,  $0P$ .

Pyroxanthin melts at  $162^\circ$ , and volatilises with partial decomposition at a higher temperature, but may be readily sublimed by careful heating in a stream of hot air. It dissolves in strong sulphuric acid with a deep purple colour, in hydrochloric or hydrobromic acid with a crimson colour, and is precipitated by water from these solutions apparently unchanged. It is quite insoluble in aqueous alkalis, and is merely carbonised by melting potash. Bromine attacks it strongly, and under certain conditions forms well crystallised products.

*Dibromopyroxanthin tetrabromide*,  $C_5H_{10}Br_2O_3.Br_4$ , is formed on adding  $3\frac{1}{2}$  parts bromine diluted with an equal weight of carbon sulphide to pyroxanthin suspended in ten times its weight of the same liquid; and on leaving the deep-red solution to itself for 24 hours, and then distilling off the solvent, the tetrabromide separates in small, brilliant, colourless triclinic prisms, which may be purified by washing with ether. When heated, it decomposes below  $100^\circ$ , with carbonisation and evolution of hydrogen bromide. It is very slightly soluble in ether and in carbon bisulphide, easily in boiling benzene or chloroform, the greater part separating out on cooling. In cold alcohol or glacial acetic acid it is but sparingly soluble, but dissolves on warming, with decomposition, forming a yellow solution. Strong sulphuric acid carbonises it on heating. Exposed to bromine-vapour, it deliquesces rapidly, forming a dark syrup which gradually solidifies over lime in a vacuum; the product does not, however, appear to be of definite composition.

*Dibromopyroxanthin*,  $C_{12}H_{10}Br_2O_3$ , is best prepared by boiling the tetrabromide with absolute alcohol, and adding zinc-dust or finely powdered antimony. It dissolves readily in hot, sparingly in cold alcohol, easily in ether or carbon bisulphide, very easily in benzene, glacial acetic acid or chloroform, and crystallises from the last-mentioned solvent in large compact twinned monoclinic crystals, which are dichroic. Strong sulphuric acid dissolves it, forming a deep blue solution from which water throws down a yellow precipitate apparently consisting of the unchanged substance. When quickly heated on platinum foil, it melts to a perfectly clear liquid, but decomposes and carbonises when the temperature is more gradually raised: hence its melting point cannot be determined. A solution of dibromopyroxanthin in carbon bisulphide mixed with bromine gradually deposits crystals of the tetrabromide. Dibromopyroxanthin does not appear to be formed in the free state by treating pyroxanthin with quantities of bromine less than sufficient to form the tetrabromide, the solutions thus obtained yielding on evaporation nothing but indefinite products.

H. W.

**Fruit of *Omphalocarpum Procera*.** By W. A. H. NAYLOR (*Pharm. J. Trans.* [3], 12, 478—480).—To determine whether the proximate principles of the *Omphalocarpum* are allied to those of the



order *Ternstroemiaceæ* or *Sapotaceæ*, the following research was undertaken :—

When dried at 54° C. the fruit loses 50 per cent., and its pericarp yields to benzene a viscid amber-coloured resin partially soluble in alcohol (sp. gr. 0.795).

The *insoluble portion* melts at 90°, and from its properties appears to be a *congener of gutta*.

The soluble portion is a pale orange- or amber-coloured resin, closely corresponding in its reactions and general characters with *fluavil*, one of the products of the oxidation of gutta-percha.

The portion insoluble in benzene is partially soluble in alcohol (80 per cent.), and this soluble portion is again only partially dissolved by alcohol (sp. gr. 0.795).

The portion insoluble in strong alcohol consists of (a) a *wax*, m. p. 59°, soluble in chloroform, ether, benzene, and cold strong alcohol, also in boiling potash, from which it is precipitated on adding an acid; (b) a *glucoside*, a yellow amorphous powder soluble in alcohol and water, and imparting to the latter a soap-like froth, but insoluble in ether; when treated with hydrochloric acid, it yields glucose and a body having the properties of sapogenin. The glucoside itself possesses properties analogous to saponin, but its greater solubility in alcohol seems to associate it with monesin.

The fruit also contains a neutral principle, to which the name *Omphalocarpin* is given, soluble in alcohol, less so in water, and still less in chloroform and ether; it crystallises from boiling alcohol in silky needles, which are free from nitrogen; treated with warm sulphuric acid it yields a rich purple-crimson colour. Besides omphalocarpin the plant contains a bitter principle resembling cinchona-red in appearance. It is insoluble in ether and chloroform, but is readily dissolved by potash, from which solution it is precipitated on addition of an acid. Finally, this fruit contains an organic acid very soluble in alcohol and water, probably malic acid.

The seeds yield a bland fixed oil capable of saponification, yielding an acid melting at 32° and soluble in ether.

No alkaloid was found in either the pericarp or the seeds.

These results lead to the conclusion that *O. procera* is more closely allied to the *Sapotaceæ* than to the *Ternstroemiaceæ*. L. T. O'S.

**Blue Colouring Principle of Thevetia Nereifolia.** By C. I. H. WARDEN (*Pharm. J. Trans.* [3], 12, 417—418).—Some kernels of the above fruit, from which the oil had been removed by pressure, were extracted with alcohol, and the thevetin, a poisonous glucoside, removed from the filtrate by concentration and filtration; the dark mother-liquor was repeatedly agitated with chloroform, then neutralised with sodium carbonate, shaken up with ether, and the dissolved ether removed by exposure to air; basic lead acetate was now added in slight excess, the dark brown precipitate filtered off, and the bulk of the lead removed from the filtrate by tannin, the last traces by sulphuretted hydrogen; the amber-coloured filtrate evaporated to dryness on the water-bath contained the pseudo-indican contaminated with thevetin and extractives. The further purification

of the pseudo-indican was not proceeded with. It is a non-crystalline bright yellow transparent and slightly hygroscopic solid, easily pulverisable. It dissolves readily in water and in ethyl, methyl and amyl alcohols. It has a neutral reaction and an unpleasant taste, but neither bitter nor acid. Concentrated hydrochloric acid produces an almost immediate bright blue coloration in its aqueous solution; the dilute acid only on heating, blue flocks separating. Glucose was detected in the colourless filtrate.

*Thevetin-blue* when dry is a dark amorphous insoluble powder. It forms a dirty brown solution in sulphuric acid, precipitated blue by water. In hydrochloric acid, it forms a bluish-green solution, not precipitated by water in the cold, but blue flocks separate on heating. It dissolves in cold glacial acetic acid, also in soda, potash, and ammonia, and is precipitated from the latter on adding an acid. It is readily soluble in ethyl and methyl alcohols, only slightly in amyl alcohol and benzene, not at all in ether, carbon bisulphide, turpentine or chloroform. Reducing agents have no apparent effect on it, but the colour is at once destroyed by oxidising agents.

In cases of poisoning by this fruit, which occur occasionally in India, the author considers that the thevetin-blue reaction, applied to the amyl alcohol extract of the alcoholic extract of the stomach or vomit, might be useful.

F. L. T.

**Two New Vegetable Dye Stuffs.** By SAVIGNY and COLLINEAU (*Chem. Centr.*, 1881, 703—704).—*Alneïn* occurs in the alder, birch, beech, &c., and especially in all plants whose sap contains gallic acid and tannin. Prepared from these plants by various processes, it is a more or less golden-yellow substance, unaltered by dilute acids; all soluble alkalis, however, increase the intensity of the dye colour. From solutions of alneïn, lead salts separate a dark brown flocculent precipitate, tin salts a salmon, iron and copper grey precipitates, the colour of which varies with the salt used. In its reactions, alneïn resembles cachou, but surpasses it in the more intense action of alkalis on it, and its greater colouring capacity; further alneïn is a pure compound, whilst cachou is a mixture of various substances.

*Ericin* occurs in the *Erica vulgaris*, but in larger quantities in the branches of various species of poplar. The intensity of the ericin colouring matter is increased by soluble alkalis. Iron salts separate from solutions of ericin a bronze-green precipitate, tin salts a golden-yellow gum, and copper salts give a green coloration. Ericin combines readily with the aniline dyes.

V. H. V.

**$\beta$ -Lutidine.** By C. G. WILLIAMS (*Chem. News*, 44, 307—308).—The author claims priority over the results of Butlerow and Wischnegradsky (*Bull. Soc. Chim.*, June, 1880), and O. de Coninck (*Bull. Soc. Chim.*, 1880, 120) on the action of alkalis on cinchonine. A further research on  $\beta$ -lutidine, one of the alkaloids obtained by the action of potash on cinchonine, has given the following results:—

*Action of Sodium.*—When  $\beta$ -lutidine is boiled with sodium, a violent reaction takes place, the mixture assumes a yellowish-brown colour,

and, after standing and being poured into water, a heavy brown oil separates out, which is soluble in hydrochloric acid, and when fractionally precipitated with platinum chloride yields six precipitates.

Precipitate.	Per cent. Pt.	Agreeing with formula.	Per cent. Pt.
I. Brown. . . . .	25.28	$2(C_{14}H_{18}N_2)HCl, PtCl_4$ , or if higher polymer is formed $(C_{28}H_{36}N_4)HCl, PtCl_4$ .	24.61
II. Fawn coloured	24.82	—	—
III.	26.40	—	—
IV.	27.57	—	—
V. and VI	30.28	—	—

I and II consist, therefore, of the di- $\beta$ -lutidine platinohydrochloride, or if a higher homologue is formed, tetra- $\beta$ -lutidine platinohydrochloride. Mono-dilutidineplatinohydrochloride  $(C_{14}H_{18}N_2)HCl, PtCl_4$ , requires 33.53 per cent. platinum, the other precipitates, therefore, appear to be mixtures of this compound with the former.

In a second preparation, the oil was separated into four fractions boiling from 180 to 300°. The last fraction (boiling above 300°) when dissolved in hydrochloric acid, yielded four precipitates with platinum chloride.

Precipitate.	Per cent. Pt.	Agreeing with formula.	Per cent. Pt.
I.	Lost	—	—
II.	24.69	$C_{28}H_{36}N_4, HCl, PtCl_4$	24.61
III.	26.48	—	—
IV.	29.60	$C_{14}H_{18}N_2, 3HCl, PtCl_4$	29.84

The formula of this last precipitate is to be confirmed by further research.

Unlike quinoline,  $\beta$ -lutidine is not polymerised by sodium-amalgam.

In presence of toluene, sodium converts  $\beta$ -lutidine into two products, a solid and a liquid. The hydrochloride of the solid gives two precipitates with platinum chloride.

Precipitate.	Per cent. Pt.	Agreeing with formula.	Per cent. Pt.
I.	25.30	—	—
II.	33.33	$C_{14}H_{18}N_2, HCl, PtCl_4$ .	33.53

The liquid gives results similar to those obtained before, 26.14 and 30.69 per cent. Pt.  $\beta$ -lutidine is, therefore, polymerised by sodium with formation of at least two substances.

*$\beta$ -Lutidine and Silver Nitrate.*—When added to silver nitrate,  $\beta$ -lutidine forms a white curdy precipitate, soluble in alcohol, from which it is precipitated by water in glittering crystals. It has the formula  $3(C_7H_9N), AgNO_3$ .

*$\beta$ -Lutidine Hydrochloride and Uranyl Chloride.*—Lutidine hydrochloride unites with uranyl chloride to form the yellow compound,  $2(C_7H_9N, HCl), U_2O_2Cl_2$ .

*$\beta$ -Lutidine Sulphate and Uranyl Sulphate.*—A yellow crystalline body,  $2(\text{C}_7\text{H}_9\text{N})\text{H}_2\text{SO}_4 \cdot \text{U}_2\text{O}_3 \cdot 3\text{SO}_4$ .

*$\beta$ -Lutidine Picrates.*—On adding  $\beta$ -lutidine to a boiling solution of picric acid, an oil separates out, which solidifies on cooling. On dissolving this mass in boiling water and leaving it to cool, yellow needles of lutidine picrate,  $\text{C}_6\text{H}_2(\text{H} \cdot \text{C}_7\text{H}_9\text{N})3\text{NO}_3 \cdot \text{O}$ , separate out.

*Action of Chlorine on  $\beta$ -Lutidine.*—By treating  $\beta$ -lutidine with iodine, and passing chlorine through the mixture at  $100^\circ$ , a reddish-brown liquid is obtained. On fractionation, the portion boiling below  $220^\circ$ , after being treated with soda and hydrochloric acid, filtered from an insoluble green substance, and adding platinum chloride to the filtrate, yields a granular precipitate of trichlor- $\beta$ -lutidine platinochloride,  $(\text{C}_7\text{H}_6\text{Cl}_3\text{N} \cdot \text{HCl}_2) \cdot \text{PtCl}_4$ .  
L. T. O'S.

**Behaviour of Cinchomeronic Acid on Heating.** By S. HOOGWERFF and W. v. DORP (*Annalen*, **207**, 219—228).—As previously shown (*Annalen*, **204**, 113), cinchomeronic acid when heated decomposes into  $\gamma$ -pyridinecarboxylic and nicotinic acids. In order to prepare large quantities, the cinchomeronic acid is heated to its melting point, and kept at this temperature until the evolution of carbonic anhydride ceases; it is then quickly distilled; the distillate is dissolved in boiling water, and on cooling, the  $\gamma$ -pyridinecarboxylic acid separates out; the mother-liquor, after one or two more separations by gradual evaporation, finally contains a mixture of the two acids; it is then evaporated to dryness, and the pulverised residue dissolved in warm absolute alcohol; hydrochloric acid gas is then passed into this solution, until it is no longer absorbed. After some time nearly the whole of the nicotinic acid separates out as hydrochloride; this is dissolved in water, neutralised with ammonia, and precipitated with copper acetate; the copper salt is then decomposed by sulphuretted hydrogen, and the nicotinic acid purified by one or two crystallisations.

The same decomposition-products can also be obtained from tri-carbopyridinic acid, but the yield is not so good.

$\gamma$ -Pyridinecarboxylic acid separates from water in crystalline masses, which by careful heating may be sublimed without melting; they melt with partial decomposition. With hydrochloric acid, a compound is formed in fine crystals belonging to the monosymmetrical system, the measurements of which agree in most points with those made by Brezina on isonicotinic acid. The calcium salt crystallises in slender needles. The platinochloride forms fine orange crystals belonging to the monosymmetrical system (according to Brezina, asymmetrical), the relation of the axes being  $1.497 : 1 : 1.602$ ;  $\beta = 74^\circ 1'$ . The crystals contain 2 mols.  $\text{H}_2\text{O}$ . From the reactions and derivatives of isonicotinic acid, prepared by Weidel and Herzig (*Monatsh. f. Chem.*, **1**, 1), it is believed to be identical with  $\gamma$ -pyridinecarboxylic acid. The nicotinic acid obtained by this process melts at  $225^\circ$ , and sublimes without decomposition; its calcium salt is soluble, and contains 5 mols.  $\text{H}_2\text{O}$ ; a platinochloride has also been obtained.  
J. K. C.

**Codeine.** By E. v. GERICHTEN (*Annalen*, **210**, 105—114).—When finely powdered codeine (dried at  $120^\circ$ ) is added gradually to excess

of phosphorus pentachloride diluted with about five times its weight of phosphorus oxychloride, a reaction takes place, with evolution of small quantities of hydrochloric acid. The product is poured into water, dissolved up, filtered, precipitated with ammonia, the precipitate dried over sulphuric acid, dissolved in alcohol, and finally recrystallised from light petroleum. It has the formula  $C_{18}H_{20}ClNO_2$ , and crystallises in beautiful colourless leaflets with mother-of-pearl lustre (m. p. 147—148, to a brown-red fluid); easily soluble in alcohol, ether, benzene, moderately in light petroleum; insoluble in water. It is precipitated from the solutions of its salts both by sodium carbonate and bicarbonate, and by ammonia, or potash solution. With dilute acids, it behaves like a weak base. When warmed with dilute hydrochloric acid, it melts to a viscid mass, and then dissolves; by concentrating this solution, a thick, viscid, colourless syrup of the *hydrochloride* is obtained, which dries to a glassy mass. The *platinochloride* ( $C_{18}H_{20}ClNO_2.HCl$ ) $_2$ .PtCl $_4$ , is a very unstable yellow precipitate becoming brown-black when dried at 100°.

By mixing 1 mol. codeine (dried at 110°) quickly with 2 to 3 mols. phosphorus pentachloride, and then bringing the mixture into phosphorus oxychloride, a violent reaction takes place, and hydrochloric acid is freely evolved; the reaction is completed by warming at 60 to 70°. Higher temperature is to be avoided, for at 100° the solution turns brown, and methyl chloride is given off: the product is poured into a large quantity of water, and ammonia gradually added, keeping the solution cool. The precipitate is purified by dissolving in hydrochloric acid, reprecipitating, &c. This base,  $C_{18}H_{19}Cl_2NO_2$ , crystallises in dense colourless (apparently) rhombic prisms, with diamond-like lustre, melting at 196—197° to a brown liquid; if heated higher, hydrochloric acid is evolved. It is insoluble in water, easily soluble in alcohol, ether, chloroform, benzene, somewhat less so in light petroleum. It is precipitated from solutions of its salts by soda or potash, by the carbonates of sodium, and by sodium acetate. When heated with soda-lime, it gives a pyridine odour.

The *hydrochloride* crystallises in concentric groups of needles, less soluble in cold water than codeine hydrochloride. It has water of crystallisation which is not completely removed at 110°. At about 160—170°, it decomposes, turning brown, and giving off hydrochloric acid. Ferric chloride colours its aqueous solution red-brown.

The *platinochloride*, ( $C_{18}H_{19}Cl_2NO_2.HCl$ ) $_2$ .PtCl $_4$ , forms light yellow microscopic needles.

On one occasion, when preparing this base from codeine, the author obtained a base crystallising from light petroleum in needles (m. p. 124°); the hydrochloride is beautifully crystalline, and melts at 180°, with decomposition at 200°; the fused mass quickly turns brown.

By treating codeine with bromine-water, the author prepared bromocodeine (m. p. 161—162°),  $C_{18}H_{19}BrNO_2$ , and by the action of phosphorus pentachloride on this body (using the method adopted in making the base  $C_{18}H_{20}ClNO_2$ ), he obtained a compound,  $C_{18}H_{19}BrClNO_2$ , crystallising in dense colourless prisms (m. p. 131°), soluble in alcohol and ether, less so in light petroleum. When heated with sulphuric acid,

it dissolves to a green-brown solution, which turns blue when poured into water, and green on the addition of alkali. With dilute acids, it behaves like the body  $C_{18}H_{20}ClNO_2$ . The *hydrochloride* is a syrup; the *platinochloride*,  $(C_{18}H_{19}BrClNO_2 \cdot HCl)_2 \cdot PtCl_4$ , forms orange-yellow flocks. This base is easily precipitated from the solutions of its salts. In a similar way chlorocodeine (m. p.  $178^\circ$ ) and nitrocodeine (m. p.  $212-214^\circ$ ) yield bases with phosphorus pentachloride, in which hydroxyl is replaced by chlorine. The base formed in the first case is not identical with the body  $C_{18}H_{19}Cl_2NO_2$ , described above.

These reactions form a fresh proof that codeine contains a hydroxyl group. D. A. L.

**Cotarnine.** By E. v. GERICHTEN (*Annalen*, **210**, 79—105).—When apophyllic acid is heated with hydrochloric acid to  $240^\circ$ , methyl is eliminated, with production of a pyridinedicarboxylic acid; it has therefore been looked upon as a monomethylpyridine dicarboxylate. The author objects to this conjecture for several reasons, and from the results of experiments, and especially the formation of the ammonium base, described in this paper and on previous occasions, he thinks that apophyllic acid is a lactide or betaine of this constitution:  $C_5H_3NMe(COOH) < \begin{smallmatrix} CO \\ O \end{smallmatrix} >$ .

*Bromotarconine* is best prepared by gradually adding an aqueous solution of cotarnine hydrochloride to hydrobromic acid containing an excess of free bromine, and drying and heating to  $160^\circ$  the hydrobromide of bromotarconine dibromide thus produced. The bromotarconine is purified by recrystallisation, &c. In this way the yield is from 18 to 20 per cent. of the pure narcotine used. Bromotarconine is a weak base; its salts are decomposed by water, and their solutions have an acid reaction. The *hydrochloride* forms long pale yellow silky needles. The *platinochloride* crystallises from hot concentrated hydrochloric acid in long silky orange-red needles.

By oxidation with chromic acid, bromotarconine gives bromoform and apophyllic acid. This shows that bromotarconine has a methyl group, and that the bromine is not in the pyridine nucleus. By the action of bromine on bromotarconine in sealed tubes at  $120^\circ$ , blue-green flocks of the hydrobromide of a base are formed, which gives a magenta solution in soda, but which is reprecipitated in insoluble brown flocks on standing, the solution at the same time being decolorised: this base was not further examined; in the filtrate from this base, bromapophyllic acid is found. By adding bromine to an aqueous solution of bromotarconine hydrochloride as long as the yellow precipitate is redissolved either on standing or on warming, and the solution is blue-green, *cuprine* is produced; if more bromine is now added, a yellow precipitate gradually forms, which remains many hours undissolved. By further addition of bromine, we obtain bromapophyllic acid, and finally dibromoapophylline hydrobromide, which is the last intermediate product between pyridine and bromotarconine in the action of bromine on the latter body.

The yellow product formed above is too unstable to be purified; it decomposes even while drying over sulphuric acid.

*Cuprine*,  $C_{22}H_{14}N_2O_6$ , separates from the deep-blue solution of its hydrobromide on adding sodium carbonate, in copper-like masses of needles, soluble in water and alcohol to green solutions, insoluble in ether. It dissolves in dilute acids with a deep-blue colour, with strong acids it gives brown-red solutions, which turn to a beautiful blue on dilution. Heated to  $280^\circ$ , it decomposes, swelling up, and giving off an odour of pyridine. It is a very weak base. Its salts are decomposed by alkaline bicarbonates, the base being precipitated in crystalline flocks, which have a copper-like lustre by reflected and a green colour by transmitted light.

The *hydrochloride* forms concentric groups of needles, which have a brownish-yellow metallic lustre, and lose water over sulphuric acid. They dissolve very readily in cold water with fine blue colour, and give with concentrated hydrochloric acid a brown-red coloration, which by gradually diluting becomes first violet and then blue. The hydrochloric acid goes off at  $110^\circ$ , leaving the dry base. The *platinochloride* is precipitated in deep blue flocks from the blue solution of the hydrochloride.

Cuprine differs from the other bases already obtained from bromotarconine, viz., tarnine, cupronine, and narceine, in its behaviour with concentrated sulphuric acid; the others are all easily attacked, whilst cuprine simply dissolves to brown-red solution, which on diluting gives first the violet and then the blue colour of the cuprine salts. On adding bromine-water to the aqueous solution of the hydrochloride, the blue colour changes to yellow. *Bromapophyllic acid*,  $C_8H_5BrNO_4 + 2H_2O$ , from the reaction described above, is purified by recrystallisation, &c.; it then forms dense colourless prisms (m. p.  $204-205^\circ$  with violent evolution of gas and blackening), which lose their 2 mols.  $H_2O$  at  $100^\circ$  and effloresce. It is soluble in hot, somewhat more so in acidulated, but only sparingly in cold water, moderately in hot, but scarcely at all in cold alcohol. It is precipitated in slender needles from its alcoholic solution on the addition of ether, and from its aqueous solution by the addition of alcohol and ether. It gives precipitates neither with silver, lead, nor copper salts, and does not give colour reactions with ferrous sulphate or ferric chloride. The *barium salt*,  $(C_8H_5BrNO_4)_2Ba + 3H_2O$ , crystallises in small white fine needles, easily soluble in cold water, from which solution it is reprecipitated by alcohol in silky-looking needles. At  $100^\circ$ , it loses the 3 mols.  $H_2O$ , and on further heating blackens, and gives off an odour of pyridine. The *platinochloride*,  $(C_8H_5BrNO_4.HCl)_2.PtCl_4$ , crystallises gradually from a moderately concentrated solution in beautiful orange-red (apparently) hexagonal tables with glassy lustre.

When bromapophyllic acid is heated with concentrated hydrochloric acid in sealed tubes at  $200-210^\circ$ , it yields carbonic anhydride, methyl chloride, and an acid which shows the following properties:—it crystallises in druses of small needles, easily soluble in hot and acidulated water, sparingly in cold. When heated, it becomes soft and decomposes; at  $199^\circ$  it melts, giving off carbonic anhydride accompanied by a pungent-smelling vapour, and the formation of an oily sublimate which soon crystallises. The aqueous solution of the acid gives a crystalline precipitate with lead acetate; with silver

nitrate, a precipitate of fine white needles easily soluble in dilute nitric acid; with copper acetate in the cold, no precipitate, but on warming, a thick pale-blue flocky precipitate which disappears on cooling. If, however, the solution of the acid with the copper acetate is left to stand, it gradually deposits after some time long light-blue needles of the copper salt of the acid, which loses 31 per cent. water at  $130^{\circ}$ , becoming at the same time blue-green. When heated with soda-lime, the acid gives off the odour of pyridine. It is probably a mono- or di-carboxylic acid of bromopyridine.

The *dibromapophylline hydrobromide* mentioned above forms druses of colourless needles of a vivid mother-of-pearl lustre (which does not disappear on drying at  $100^{\circ}$ ); on boiling with barium carbonate, it yields the free base.

*Dibromapophylline*,  $C_{14}H_{10}Br_4N_2O_4 + 4H_2O$ , crystallises in large colourless hexagonal tables, easily soluble in hot and cold water, but very sparingly in ether; the aqueous solution has a neutral reaction. When heated to  $90$ – $100^{\circ}$ , the crystals effloresce and lose their water, undergoing a slight change, and when dried quickly (at  $100$ – $110^{\circ}$ ) the edges of the crystals always appear of a faint brown colour; at  $215$ – $220^{\circ}$ , they become brown, then black, and melt at  $229^{\circ}$  to a black fluid with evolution of gas. It gradually colours boiling alkaline solutions an intense brown-red, and causes turbidity. If freshly precipitated silver oxide is used in the preparation of the base from the aqueous solution of its hydrobromide, part of the oxide goes into solution, and on concentrating this, metallic silver is deposited. It forms neutral and basic salts. The former are converted into the latter by boiling with water. The *neutral hydrobromide* crystallises from strongly acid solutions in tetrahedral crystals, which when boiled with water are converted into needles of the basic salt (*ante*)  $C_{14}H_{10}Br_4N_2O_4 \cdot HBr$ ; this is easily soluble in cold water, very slightly in alcohol, and insoluble in ether, by which it is precipitated from its alcoholic solution in slender needles. It dissolves in soda, forming a colourless solution, which turns red on boiling. Like the base, this salt becomes slightly brown by prolonged heating at  $100^{\circ}$ . When the heating is continued at about  $170^{\circ}$ , it begins to decompose and becomes soft; at  $190$ – $192^{\circ}$  it begins to melt with much frothing, and at  $204$ – $205^{\circ}$  it is quite fused. When it is heated in a small glass tube below  $180^{\circ}$ , a sublimate of beautiful long needles of dibromopyridine (m. p.  $109$ – $110^{\circ}$ ) forms, carbonic anhydride and methyl chloride being evolved. The residue in the tube is methyl-dibromopyridylammonium hydroxide, described below.

*Neutral dibromapophylline hydrochloride* crystallises from concentrated hydrochloric acid in large rhombic tables free from water of crystallisation. It is very unstable, gives off hydrochloric acid in damp air, and by boiling with water is converted into needles of the *basic hydrochloride*,  $C_{14}H_{10}Br_4N_2O_4 \cdot HCl$ , which is similar in properties to the hydrobromide.

The *platinochloride*,  $(C_{14}H_{10}Br_4N_2O_4 \cdot HCl)_2 \cdot PtCl_4 + H_2O$ , crystallises in splendid orange-red monoclinic prisms, losing their water at  $100$ – $105^{\circ}$ , slightly soluble in cold, moderately in hot water; insoluble in alcohol, and easily soluble in warm dilute hydrochloric acid. The



*nitrate* forms clear colourless dense prisms; the *sulphate* long colourless needles, somewhat less soluble than the hydrochloride.

When heated with hydrochloric acid in sealed tubes at 140—150°, dibromopophylline undergoes a change, which, however, is only complete at 180°, carbonic anhydride, methyl chloride, dibromopyridine, and the hydrochloride of the above-mentioned ammonium base being produced; at 200—210° a complete breaking up even of the ammonium base takes place, the products being the first three substances only. During these changes, the liquid remains quite colourless.

*Methyldibromopyridylammonium hydroxide*.—The *chloride* crystallises in dense colourless leaflets, very soluble in water, sparingly in alcohol, insoluble in ether. By digesting the aqueous solution with silver oxide, a colourless liquid with a strongly alkaline reaction is formed, which in a short time becomes reddish, and on warming intensely red, with slightly violet tone, and the gradual separation of a red-brown oily product. With soda, the decomposition takes place more quickly. When it is boiled, a pungent vapour is given off, which resembles that of dibromopyridine: a yellowish oily base can be extracted with ether from the alkaline (decomposed) solution. The *bromide* decrepitates when heated on platinum-foil, but in a tube it remains white until near 250°, when it begins to decompose into methyl bromide and dibromopyridine; between 260—270°, it is completely volatilised. The *platinochloride*,  $(C_5H_3Br_2N.CH_3Cl)_3PtCl_4$ , forms orange-red glistening leaflets, soluble in cold, and very easily in hot water, insoluble in cold, and very sparingly soluble in hot alcohol. The properties of the free base agree with those given by Anderson (*Annalen*, **94**, 358) and Hofmann (*Ber.*, **14**, 1498) for the pyridyl-ammonium bases. To prove the identity with methyldibromopyridyl-ammonium hydroxide, some of this base was prepared synthetically, and its properties were found to agree perfectly with those above described.

The *dibromopyridine* obtained in the decomposition of dibromapophylline is identical with that obtained by Hofmann (*ibid.*, **12**, 988).

D. A. L.

**Peculiar Alkaloid from Cinchona Cuprea.** By B. H. PAUL and A. J. COWNLEY (*Pharm. J. Trans.*, **12**, 497).—The bark of the *Cinchona cuprea* yields a substance, which separates from the ethereal solution of the alkaloids in long thin plates, and sometimes in needles. It forms a sulphate sparingly soluble in water, thereby differing from cinchonidine and quinidine, but resembling quinine, from which it is distinguished by its slight solubility in ether; its tartrate, however, resembles cinchonidine tartrate by its sparing solubility in water.

It is not all samples of cuprea bark which give indications of the presence of this alkaloid.

L. T. O'S.

**New Alkaloid from Cinchona Cuprea.** By W. G. WHIFFEN (*Pharm. J. Trans.*, **12**, 497).—The results obtained confirm those detailed in the preceding abstract. It is further stated that the bark contains from 0.1 to 0.8 per cent. of the alkaloid, which is very soluble in alcohol and dilute ammonia, and has a strongly alkaline reaction. Neither cold sulphuric acid nor concentrated nitric acid decomposes

it, but with sulphuric acid and potassium dichromate it gives a deep green coloration, and with chlorine-water and ammonia an emerald-green coloration. It is precipitated from its aqueous solutions by rochelle salt, but not by potassium iodide when cautiously added. Its acid sulphate is highly fluorescent, and has a higher rotatory power than quinine sulphate.

Cinchonidine sulphate . . . . .	$[\alpha]_j = -135^\circ$
Quinine sulphate . . . . .	$[\alpha]_j = -196$
Sulphate of new base . . . . .	$[\alpha]_j = -221$

The author suggests the name of "Ultra-quinine" for this alkaloid until its properties have been further studied. L. T. O'S.

**Fresh Occurrence of Aricine and Cusconine.** By O. HESSE (*Pharm. J. Trans.*, 12, 517).—With regard to the new alkaloid in the bark of the *Cinchona cuprea* (preceding abstracts), the author has found in the same bark, besides aricine, cusconine, and some cinchonine, a small quantity of an alkaloid greatly resembling cinchonidine, but in many points essentially differing from it. His results will be published shortly. L. T. O'S.

**Contribution to the Examination of Pilocarpine and its Salts.** By A. CHRISTENSEN (*Pharm. J. Trans.* [3], 12, 400).—Several samples of pilocarpine and its salts were submitted to the author for examination. No differences were observable qualitatively. In endeavouring to estimate the alkaloid quantitatively, the author found Poehl's method of precipitating with phosphomolybdic acid highly unsatisfactory: the author finally estimated it by means of the aurochloride,  $C_{23}H_{34}N_4O_4(HCl.AuCl_2)_2$ . The chemical examination showed practically no difference, but the physiological experiments showed a marked difference, two samples being more active than pilocarpine, and resembling jaborine and atropine. F. L. T.

**Behaviour of Unorganised Ferments at High Temperatures.** By F. HÜPPE (*Chem. Centr.*, 1881, 745—746).—As Bull has shown that emulsin can be heated even to  $100^\circ$  without destroying its fermenting activity, the author has examined the behaviour at high temperatures of pepsin, malt-diastase, trypsin, and the diastatic ferment of pancreatin. These preparations were dried over sulphuric acid, and then heated for various lengths of time: it was found that dried pepsin could be heated to  $170^\circ$ , malt-diastase to  $158^\circ$ , and the pancreatic ferment to  $162^\circ$ ; the author fixes  $170^\circ$  as the limit of temperature at which ferments can be heated without being impaired. The author's results are in agreement with those of Salkowski, but in opposition to those of Finkler—that ferments, whether heated or not, form the same products under the same conditions, and that no quantitative differences can be observed after heating to  $100^\circ$ . However, after heating to  $100^\circ$  less albumin was peptonised and less starch inverted, and moreover pancreatic ferment, heated to  $100^\circ$ , gave 10.5 and 2.02 per cent. maltose from starch, but, if not heated, 12.8 and 3.2 per cent. maltose, the conditions in all cases being the same. It follows, as a

practical result, from these experiments, that dry unorganised ferments at the usual temperature of disinfecting reagents, are not destroyed with certainty; but in the moist state the temperature of boiling water is sufficient for their destruction. These experiments are of importance for hygiene, inasmuch as experiments, with a view of finding the causes of infectious diseases and micro-organisms, have hitherto been unsuccessful; and it is still an open question as to what part unorganised ferments play in their destruction. V. H. V.

**Presence of Peptones in Plants.** By E. SCHULZE and J. BARRIERI (*Chem. Centr.*, 1881, 714—720, 731—736, 747—752, and 761—765).—As Gorup-Besanez has demonstrated the existence of albumin solvent ferments in the seeds and other parts of plants, the presence of peptones was to be expected; but experiments with a view of finding these substances have for the most part been unsatisfactory. On the one hand, Kern has found peptones in the extracts of fodder plants, lucerne, vetches, &c., but considers that they were formed during the preparation of the extracts. On the other hand, Kellner maintains that peptones are neither present nor are formed during the process of extraction, if sufficient care be taken. The authors have re-examined the question by the light which the researches of Hofmeister have thrown on the chemical nature and properties of peptones; they have also adopted the methods of separation (*Abstr.*, 1879, 183) and the so-called biuret reaction (*i.e.*, red-violet coloration with copper sulphate in alkaline peptones) proposed by Hofmeister. This latter reaction forms a basis for a colorimetric determination of peptone, a number of solutions of standard tints being prepared by dissolving known weights of peptone (from blood fibrin), and adding to them known volumes of soda and copper sulphate solutions. In order to isolate peptone from vegetable extracts, the authors, adopting the method of Ritthausen, have treated the albuminous substance known as conglutin (obtained from lupines) with pepsin solution, and purified the product by the processes used for fibrin peptone. This preparation was not so pure as ordinary fibrin peptone, resembling the latter in its behaviour towards tannin and phosphotungstic acid, but differing from it in giving a precipitate with acetic acid and potassium ferrocyanide. The coloration produced from the plant-extract with copper sulphate was of the same tint as that formed with a solution of fibrin peptone of strength 1 : 1000. Similar results were obtained with other extracts, and the authors have thus demonstrated the existence of peptone in plant-buds, seeds, potatoes of various species, and in the sap of beetroot, but in all cases in relatively small quantities. In many of the fodder grasses, no peptones were found, but an examination of young plants showed that there were present ferments which, in the course of the preparation of the extracts, acted on the albumins and converted them partly into peptones. Further, it was shown that, using suitable methods of extraction, the formation of peptone can either be entirely prevented, or at least modified. An examination of lupine seeds revealed the presence of a substance intermediate between albumin and peptone, similar to the substance obtained by Vines (*Abstr.*, 1881, 1062), and named by him vegetable peptone. From its

properties the authors consider that it cannot be classed as a peptone, but only as a transition substance, resembling the peptone of Schmidt Mülheim. As it was found that in many plant-extracts obtained from various sources, only a small fraction of the nitrogen constituents of the phosphotungstic acid precipitate arises from the peptone, it is probable that a more intimate examination of this precipitate would lead to the isolation of nitrogenous substances; and in an added note the authors suggest that these probably belong to the xanthin class, which have recently been found by Salomon in plant-seeds.

V. H. V.

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## Physiological Chemistry.

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### **Influence of Irregular Work on Digestion of Food by Horses.**

By E. VON WOLFF and others (*Bied. Centr.*, 1881, 607—612).—This is a summary of experiments by various investigators on the influence of varying amounts of work by horses, when they were regularly fed; the results, which are fully stated, confirm previous experiments made at the experimental station of Hohenheim, that when horses are regularly fed, the digestion of their food is constant and regular. The fodders experimented on were meadow hay, oats, and rice flour, linseed, and linseed cake. J. F.

**The Diastatic Action of Saliva.** By R. H. CHITTENDEN and W. L. GRISWOLD (*Am. Chem. J.*, 3, 305—316).—I. *Influence of Acids, Alkalis, and Gastric Juice on the Diastatic Action of Saliva.*—Human mixed saliva, when freshly secreted, has usually an alkaline reaction. The saliva of the parotid gland, however, which contains the greater part of the diastatic ferment, has, according to Astaschewsky, a very faint acid reaction, which gives place to an alkaline reaction when the mucous membrane of the mouth is strongly irritated. According to the same authority, the maximum of the diastatic action of parotid saliva corresponds with the strongest acid reaction. Other investigators, on the contrary, state that the diastatic action of saliva is entirely destroyed by acids, whereas alkalis do not interfere with it. Great diversity of opinion exists also on the effect of acid of the strength of the gastric juice on saliva, when the two fluids are mixed in the stomach during normal digestion.

With the view of obtaining more exact results, the authors have made a series of experiments, in such a manner as to secure uniformity in the various steps of the process; while at the same time each experiment served as a check by means of which the diastatic action of the acid or alkaline saliva could be compared with that of normal saliva of the same collecting, thus affording the means of accurately measuring the influence of the acid or alkali on the diastatic action.

The method employed was as follows:—1 gram of starch was made into a paste by boiling with 25 c.c. water; then, after cooling, 50 c.c.

of the diluted acid or alkali were added, and, finally, 25 c.c. of filtered human saliva; while in the check experiment, 50 c.c. water were added in place of acid or alkali; so that the dilution was the same in each case. The mixtures were placed in a water-bath at 38—40° for a definite time, usually 45 minutes, and occasionally stirred; the liquid, after neutralisation, was quickly boiled to destroy the ferment; then diluted with water to 500 c.c.; after thorough mixing, 50 c.c. of this liquid were filtered from unchanged starch; and in this one-tenth, the sugar and other reducing substances were determined, either gravimetrically, by Maercker's method (*Landw. Versuchs.-Stat.*, **25**, 115), or by titration with Fehling's solution.

The results of these experiments show that the presence of acid to the amount of 0.005 per cent. decidedly increases the diastatic action, while an increase of acid beyond this percentage diminishes it in a very marked degree. With stronger solutions of acid (0.1, 0.2, and 0.4 per cent. HCl) the action was wholly stopped. The increase in the amount of sugar formed in a faintly acid solution (0.005 per cent.) tends to corroborate the statement of Astaschewsky (*Centr. f. Med. Wiss.*, 1878, p. 15), that the maximum of the diastatic action of parotid saliva corresponds with the strongest acid reaction.

The diastatic action is somewhat diminished by the addition of *sodium carbonate*, but is not further affected to any material extent by an increased percentage of the alkali. The fluids of the intestinal canal are distinctly alkaline; the pancreatic juice, which is most actively concerned in the chemical actions occurring in the intestines, is likewise strongly alkaline, containing presumably an amount of alkali equivalent to 0.3 per cent.  $\text{Na}_2\text{CO}_3$ . The experiments show, therefore, that an alkaline solution, of the strength most favourable to the digestive action of trypsin, does not impede to any great extent the action of the ptyalin of pancreatic juice, whilst any salivary ptyalin that may have survived the action of the gastric juice would again be active under the conditions of the intestinal canal.

With respect to the probable effect of a mixture of saliva and gastric juice, respecting which conflicting opinions are entertained, the authors find that the diastatic ferment of saliva is not only hindered in its action by the acidity of the gastric juice, but that it is, in part at least, destroyed, and thus debarred from any further part in the conversion of starch into sugar.

II. *Products of Salivary Digestion.*—In order to study in detail the different products which result from the action of saliva on starch, 40 grams of starch made into a paste by boiling with 600 c.c. water were digested with 200 c.c. filtered saliva for fifteen hours at 10°, and the semi-dry residue left on evaporation over a water-bath was treated for 24 hours with 700 c.c. alcohol of 90 per cent. The substance then remaining was composed mainly of unaltered starch, but contained also a body of strong reducing power and, apparently, dextrorotary. On treating the alcoholic solution with 300 c.c. ether, and leaving it at rest for several days, a gummy precipitate settled out; and, after repeating this treatment with ether three times, a precipitate gradually settled down, consisting wholly of small white needle-like crystals having the composition  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , and exhibiting all the

characters of maltose. This result agrees with that of Musculus and Mering (*Zeitschr. Physiol. Chem.*, **2**, 403), also with that of Bimmermann and Kulz (*Pflüger's Archiv*, **20**, 201).

The last alcohol-ether filtrate from the maltose precipitate left on evaporation a small quantity of a dextrorotary body possessed of strong reducing power, probably dextrose. The three syrupy or gummy precipitates obtained previous to the maltose, were also dextrorotary and possessed of reducing power. H. W.

**Fodder Experiments on Milch Cows with Cotton-seed Meal and Peanut Meal.** By H. POGGE (*Bied. Centr.*, 1881, 612—615).—One of the faults of peanut cake is that the quality varies within wide limits, owing to the liability of the nuts to become rancid during their long transit by sea. Cotton-seed cake on the contrary keeps very well.

The animals on which the experiments were made as to the value of the respective cakes, were two lots of 10 cows each, chosen with great care, so that both should be equally suitable; the first lot was fed on peanut cake for a period of 15 days, and then on cotton-seed meal for the same length of time; the second lot commenced with the cotton-seed and finished with the peanut cake.

The analyses of both foods are given—

	Cotton-seed meal.	Peanut cake.
Moisture .....	8.50	9.80
Protein matter .....	41.50	48.25
Fat.....	16.67	8.57
Cellulose .....	7.78	5.26
Non-nitrogenous extract ....	18.39	23.69
Ash.....	7.16	4.43

1 kilo. of each was given along with the usual fodder of the animals, the cotton-seed meal was much relished.

From a tabular statement of the average milkings, it appears that the substitution of cotton-seed meal for the peanut cake was followed by an increase in the yield of milk, but on the second lot of cows the alteration did not occasion any increase. Samples of butter were made five times during each period; during the feeding on peanut cake, it required 34.21 litres to produce 1 kilo. of butter; during the cotton-seed period, it required but 31.18 litres to the kilo. of butter; the flavour of both was equally good. The results of the experiments were favourable to the peanut cake, but not sufficiently so as to cause the author to recommend its substitution for cotton-seed meal.

J. F.

**Influence of Different Oil Cakes on Milk Production.** By THREADWELL (*Bied. Centr.*, 1881, 615—617).—Experiments were made by Threadwell on the effects of decorticated cotton-seed alone, and the same mixed with malt, as fodder for milch cows. Eleven animals were selected, to each of which 2 kilos. of the cotton cake were daily given, together with hay and sliced beet. After some days, 1 kilo. of the cake was replaced by  $\frac{1}{10}$ ths of a litre of malt, and still later the

cake was discontinued altogether, and 1·2 litre of malt given instead. On comparing the yield and quality of the milk during the three periods, and the relative cost of the two articles of food, the mixture of cotton-seed cake and malt was found the most advantageous, and Threadwell has put all his cattle and horses on this diet with great success.

The other experiments were made at the Netherlands Veterinary School on the influence of linseed cake and malt combings cake on milk production; five cows were experimented on, and they received each 2 kilos. of cake in addition to their other food. The quantity of milk was very closely the same during both periods of feeding, but the quality as shown by analysis was rather in favour of the linseed, but not materially so. The butter, milk, and cheese produced by the malt combings cake were of most excellent taste. The following are the analyses of the two milks:—

Cake.	Water.	Fat.	Milk-sugar.	Casein.
Malt combings ..	86·35	4·40	4·13	5·12
Linseed .....	85·91	4·56	4·01	5·52
				J. F.

**Physiology of Sugar in the Animal System.** By F. W. PAVY (*Proc. Roy. Soc.*, **32**, 418—432).—The author has conducted a series of experiments in order to re-examine the validity of the glycogenic theory, which supposes the transformation of glycogen into sugar by contact with blood. Known weights of glycogen were dissolved in water, and the solutions added to known volumes of defibrinated blood. The mixture was then heated to 100—110° F., the normal temperature of the body; under these conditions, the merest trace of sugar was produced, which proves that glycogen is not to any appreciable extent transformed into sugar when in contact with the blood. The author has succeeded in demonstrating the existence of a substance probably identical with glycogen in the blood itself; for by treating blood with potash, and pouring the product into alcohol, a solution was obtained which possessed no cupric oxide reducing power, although the solution on treatment with sulphuric acid and subsequent neutralisation, showed a cupric oxide reducing power, due to conversion of the glycogen into glucose by the acid. It was found that as a mean of 29 results with the blood of sheep, bullocks, cats, rabbits and horses, 1000 parts of blood contained '616 of glycogen. Glycogen is also shown to exist, not only in the muscle, but also in notable amount in the spleen, pancreas, kidney and brain, and in the white and yolk of eggs; there is also present in these various organs and substances, a cupric oxide reducing matter, which possesses, in the case of muscle, the characteristic properties of maltose. Glycogen occupies a position in the system parallel to albumin, in that it exists in the colloidal state, and is thus adapted for retention within the body, instead of passing off like the diffusible glucose. V. H. V.

**Relation of White Blood Corpuscles to the Coagulation of the Blood.** By L. C. WOOLRIDGE (*Proc. Roy. Soc.*, **32**, 413—418). The author has conducted a series of experiments to investigate the



part played by the white corpuscles in the coagulation of the blood in order to bring in accordance the views of Schmidt and the more recent researches of Hammarsten. According to the generally received theories, the white corpuscles on leaving the body die, and in consequence break up into fibrin ferment and paraglobulin, the fibrinogen being pre-existent in the plasma. The essential element in the coagulation is therefore the death of the white corpuscles. The results of the author's experiments are, however, in direct contradiction to these views: the blood removed from a peptonised dog coagulated only on the addition of lymph-cells; after removal of this test blood, a quantity of dead lymph-cell suspended in salt was injected into the animal, and a *post mortem* examination revealed no coagula.

These facts show that coagulation is a result of change in the plasma, and that the conversion into fibrin is quite independent of any pre-existing fibrinogen substance. This latter statement is also confirmed by a study of the behaviour of lymph-cells towards plasma, which indicate that the substance produced, when peptone plasma is the destroying agent, is fibrin, and that this owes its origin to a simple transformation of the protoplasm of the leucocytes.

V. H. V.

**On the Origin and Prevention of Splenic Fever.** By PASTEUR and others (*Bied. Centr.*, 1881, 499—604).—This is a report from French sources of the experiments of Pasteur, assisted by Roux and Chamberlain, on the protective action of his artificially prepared solutions against the fatal results of splenic fever in cattle. He had already demonstrated the part played by earthworms in bringing to the surface of the fields the spores of the bacteria of this disease developed in the bodies of animals which had died of it and been buried there. Toussaint, Professor at the Veterinary School of Toulouse, had about the same time experimented on another mode of protecting sheep from it by importing and breeding from an Algerian stock, which enjoys immunity from it. Chaveau, in his experiments on Barbary sheep, proved that the breed survived four or five inoculations at brief intervals, after which they were proof against injection even of the blood of animals dying of the disease.

Koch and Oemler in Germany had about the same time published researches on the subject, which the French investigators ignore. Toussaint, besides his experiments on Algerian sheep, had tried others on French sheep, dogs, and rabbits, in the hope of obtaining a protective lymph. He proceeded by removing the fibrin from the blood of a sick animal, and either heating it to 52°, or adding to it carbolic acid in a quantity not stated; with this blood he inoculated six out of a flock of 11 wether sheep; at the end of a few days the whole 11 were inoculated with the unaltered blood of cattle which had died from the fever. The six sheep which had been protected by previous inoculation survived, the others died. The same thing happened with dogs of six months—very susceptible to infection at that age. Lambs, whose dams had been inoculated with the prepared blood in the last month of their bearing, enjoyed complete immunity when inoculated with the unaltered blood.

Pasteur's experiments on the protective solutions in chicken cholera

gave an immense impetus to research in this direction, his own investigations, however, being of the greatest interest. The most important series of experiments made by him on the subject of splenic fever were the results of an arrangement made with the Agricultural Society of Melun, by which that Society placed at his disposal 60 sheep and 10 cows for experimental purposes. The arrangements for the experiments were prepared on an exhaustive scale. The following is their order:—

1. 10 sheep were to be set aside and not subject to any experiment, serving as control.

2. 25 sheep were to be inoculated twice at intervals of 12 to 15 days with the dilute virus.

3. 25 sheep which were not inoculated were to be, together with the other 25 which had been inoculated, infected with the most virulent fever poison procurable, the expected result being the survival of the 25 which had been protected, and the death of the others.

4. Comparison of the survivors with the 10 control sheep in No. 1 to show how quickly they regain their normal condition.

5. Stabling the two lots of 25 each in the same stable to allow full scope for infection.

6. Stabling the control 10 sheep in a distant stable to avoid infection.

7. Burial of the dead sheep in separate graves at a little distance from each other, and carefully fencing the plot where they were interred.

8. In the month of May, 1882, 25 fresh sheep, not subjected to any previous experiment, are to be grazed in this enclosure, and after eating the grass to be fed on clover cut from the plot.

9. 25 fresh sheep to be penned in another field a few meters distant from the enclosure where the bodies were buried.

This exhaustive programme was commenced on 5th May of this year, and all its arrangements, except Nos. 8 and 9, carried out in presence of numbers of agricultural and scientific assistants; the results were exactly as predicted by Pasteur, all the sheep protected by inoculation lived, except one ewe in lamb, which on being dissected was found to contain a decomposed foetus. All those not so protected perished; four cows unprotected were violently attacked, but recovered. The prevention of splenic fever by means of inoculation is therefore a success. The mode of preparing the protective lymph has however not yet been published. J. F.

**Chicken Cholera.** By PASTEUR (*Bied. Centr.*, 1881, 605—607).—The fatal disease known as chicken cholera was thought by Moritz, a veterinary surgeon in Alsace, to be caused by a microscopic organism; this was confirmed by Peronsito, of Turin, another veterinary surgeon, and settled beyond doubt by Toussaint, Professor at the Veterinary School in Paris.

Pasteur inoculated healthy fowls which had never had the sickness with virus from some who had died of it; they all died. He then inoculated another lot with diluted virus; none of these died, but all were sick; after a few days he treated them with the undiluted poison,

14 out of 20 succumbed. This led to repeated experiments, from which he found that repeated inoculations with the dilute matter gave perfect immunity. He then attempted, with success, the artificial propagation of the organism, using a decoction or broth of fowls' flesh, malt extract, in which the organisms of splenic fever multiply with facility, being unsuitable. Fowls fed on meat or bread mixed with the artificial preparation, take the sickness through the intestinal canal. Guinea-pigs inoculated are not killed, but an abscess appears at the place of inoculation. Hens when inoculated with the matter from the abscess of the guinea-pig died, and both rabbits and fowls placed in the same inclosure with the guinea-pigs took the disease and died of it, the abscesses ripening and breaking having communicated it by contact. Pasteur has by his experiments demonstrated that immunity from this disease can be attained by frequent inoculations with artificially prepared solutions. He believes that this is due to the organisms introduced by inoculation exhausting the substances in the body which afford them nourishment, and that when the animal is attacked by the real cholera, the organisms, however introduced, find no food and perish. The contrary theory of Grawitz is that in the struggle of the animals' system against the introduction of the poisonous matter, it becomes fortified, new growth of cells takes place, and when the animal is again attacked by the disease naturally, the system is able successfully to resist its consequences. J. F.

**Occurrence of Phosphorus-bases in the Urine, &c., in Acute Phosphorus Poisoning.** By F. SELMI (*Arch. Pharm.* [3], 19, 276—292).—Two cases of poisoning by phosphorus, one ending fatally, furnished the materials. The urine, with the exception of that first passed in the case that recovered, was found in both cases to give off in the cold a phosphorus vapour which blackened silver-nitrate paper.

Bodies behaving towards nascent hydrogen like the lower oxides of phosphorus were present in the urine, especially in the fatal case. They decreased, without however disappearing, under the administration of oil of turpentine.

A neutral volatile phosphorus compound, apparently partially formed by the action of heat, occurred in the urine in both cases.

The phosphines occurred in the urine only to a small extent in the fatal case, but in the other case were present in abundance. In the fatal case, ammonia and the lower oxides of phosphorus were largely present. The phosphines appear to alter in their character according to the time of elimination, the amount of phosphorus being larger in the later than in the earlier periods; but according to the physiological experiments of Ciaccio, the poisoning power of those first eliminated is greater than that of those eliminated after administration of oil of turpentine. Two volatile phosphines were found constant, the one being far more easily dissociated from its salts than the other.

The liver and the brain were also both examined. In the brain there were one volatile and two fixed phosphines, all richer in phosphorus than those occurring in the urine. The volatile phosphine in the brain was less poisonous than those in the urine, but the fixed were far

more poisonous. There was also found in the brain a combination of cholesterin with a phosphorus compound, which yielded phosphorretted hydrogen on treatment with nascent hydrogen.

From the liver, three phosphorus bases were also obtained, different from those found either in the urine or in the brain; two were volatile, and were very rich in phosphorus; of these one had an odour very similar to that of conine. In the liver, no acid was found yielding phosphorus to nascent hydrogen, thus contrasting it with the brain.

The author considers that the phosphines are very important in toxicological cases, especially where the corpse has been long buried, and all free phosphorus must have disappeared. F. L. T.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Influence of the Electric Light on Vegetation.** By C. W. SIEMENS (*Proc. Roy. Soc.*, 30, 210—219, and 293—295).—The author at the outset contrasts the actinic effect of the rays of the sun or electric light with that of furnace-fire, and from this it appears probable that the electric light, rich in actinic rays, would promote the development of vegetation by the dissociation of water and carbonic acid, and formation of chlorophyll and starch. In order to examine the effect of the electric light on the growth of plants, sets of pots were planted with quick-growing seeds, and divided into four groups, of which one was kept entirely in the dark, the second exposed to the electric light only, the third to sunlight only, and the fourth to daylight and the electric light successively. In all cases the fourth group were the most vigorous, and the green of the leaf was of a richer hue.

From these and similar experiments, the author arrives at these conclusions:—(1) That the electric light promotes growth, and the production of chlorophyll in the leaves of plants; (2) that an electric centre of light equal to 1400 candles at a distance of 2 metres from growing plants is equal in effect to average daylight; (3) that carbonic acid and nitrogen compounds generated in the electric arc have no injurious effects on plants; (4) that plants do not require a period of rest, but progress favourably if exposed during the night to the electric light; (5) that the radiation of heat from the electric arc can counteract the evil effects of night frost. It has also been observed by Schübeler that plants grow continuously under the effect of uninterrupted sunlight in the Arctic regions.

In the second communication, the author shows that the electric light may be rendered serviceable not only for the development of the leaves, but also for the ripening of fruit.

V. H. V.

**Water Distribution in Plants.** By G. KRAUS (*Bied. Centr.*, 1881, 630—632).—The sap of certain plants was expressed and filtered, and the sp. gr. taken with the usual precautions; it varied between 1·03 and 1·0059; the plants were *Lonicera tartarica* and *Datura*. The juice of sugar-beets ranged between 1·057 and 1·074. The sp. gr. of the sap in the growing twig was found to be less in the older than in the younger portions, and growth was invariably accompanied by dilution of the sap owing to constantly increasing absorption of water. The free acids and albumin also decreased in percentage, but increased in actual quantity. The increase in sugar during growth was remarkable; it increased with great rapidity up to a certain point, when it again declined, so that there is a maximum point in sugar contents which is not at all coincident with the maximum of growth.

An extended series of observations shows that in crooked plants the under or convex side contains sap of less concentration, and poorer in free acid and sugar, not only relatively but absolutely. Horizontal branches are richer in sugar than vertical. When plants are shaken so as to bend their tops towards the ground, an immediate increase of sp. gr. in the sap, and an increase of sugar in the under or convex part of the bend takes place, showing that the sugar is in actual process of formation at the time of bending. J. F.

**The Physiological Signification of Transpiration in Plants.** By F. REINITZER (*Bied. Centr.*, 1881, 626—627).—Many plants give off large quantities of water by transpiration, and it is generally believed that the process facilitates the absorption of inorganic nutritive matter from the soil; this theory cannot, however, be reconciled with the fact that plants thrive luxuriantly when means are taken to prevent transpiration. The author put the matter to the test of actual experiment by placing specimens of *Tradescantia viridis*, *Boussingaultia*, and *Euonymus japonica* under bell-glasses (the flower pots excepted); he submitted one to a current of dry air, another to a supply of water under high but constant pressure. The results were conclusive: the plants which did not transpire were threefold richer and of more luxuriant growth than the specimen in dry air, transpiration evidently delaying the progress of growth. Plants, like the cactus tribe, which grow in hot, arid situations, protect themselves by thick fleshy surfaces. The transpiration of moisture, however, seems to promote the growth of *wood*, but is not essential, as wood is produced in hot-houses where the air is artificially moistened. J. F.

**Decomposition of Nitrates during Vegetation in the Dark.** By BOUSSINGAULT (*Bied. Centr.*, 1881, 627—628).—The author found that samples of barren soil, treated with potassium nitrate and used to grow beans in the dark, lost in an unaccountable manner a large proportion of the added nitrogen; the only hypothesis tenable under the circumstances was, that the roots of the plants produced a substance which acted on the acid of the nitrate, and set the nitrogen free in the gaseous state. To settle the point, Müntz undertook an experiment with ignited sand, treated with hydrochloric acid. Two portions of 200 grams each were placed in flasks and moistened with distilled

water. In one, were placed some grains of maize already germinated; the other contained sand and water only; they were placed under the same bell-glass in a dark place and left for 17 days, at the end of which time the plants, with every particle of their roots, were carefully removed. Microscopically examined, both samples were quite alike, containing no other organisms than a few micrococci; but when heated in a sealed tube, the sample which had not contained plants remained perfectly white, whilst the other became slightly blackened. The author concludes, therefore, that the roots had parted with some organic substance, which had the property of decomposing nitrates.

J. F.

**Thevetia Nereifolia.** By J. E. DE VRIJ (*Pharm. J. Trans.* [3], 12, 457).—The author finds (contrary to a statement on p. 397 of the above Journal) that the kernels of the seeds of this plant contain rather more than 35·5 per cent. of a perfectly limpid, almost colourless oil, with a very agreeable mild taste, equal to that of fresh oil of almonds (sp. gr. 0·9148 at 25°). It becomes pasty at 15°, and is entirely solid at 13°. A. C. Oudemans found it to consist of 63 per cent. of trioleïn, and 37 per cent. of tripalmitin and tristearin. After the expression of the oil, the cake yielded 4 per cent. of thevetin. 1·14 grams of thevetin, dissolved in glacial acetic acid up to 10 c.c., produced a lœvogyration of 9·75°.

F. L. T.

**Enemies of the Vine.** By A. BOUCHARD and others (*Bied. Centr.*, 1881, 623—626).—This paper is a summary of different experiments and observations on vine pests and proposed remedies. Bouchard describes the anthracnose, or *Sphaceloma ampelinum*, as covering the branches with black patches, extending to the grapes; from the latter it could, however, be washed off. He tried the ordinary mode of sulphuring without success; he found that a 10 per cent. mixture of sulphuric acid employed to wash the vine stalks in February prevented a recurrence of the attack, without in any way injuring the yield of the vines. F. v. Thumen reports a very early appearance of the *Perenospora viticola* in Algiers, and describes a newly-discovered enemy, which appears as gelatinous swellings on the roots, and is caused by the nematod *Anguillula Radicicola* (Greef). J. Nessler recommends, as a preventative of the hay or sour-worm, that every particle of dry wood should be burned, and the vines treated with an insect poison of his own composition, consisting of soft soap, 40 grams, tobacco extract 60 grams, fusel oil 50 grams, spirits of wine 2 decalitres; the whole diluted to 1 litre, and applied to the buds and blossoms. Schmidt contributes some notes on the same insect. The pupæ are generally found in the dead wood of the stock, never in the soil; but in default of the old wood, they will attach themselves to any firm object, and creep into hollow twigs; the district where the observations were made is very bare of trees and birds, and he thinks frosts in early spring and late warm summers, with heavy rains during the time the insect leaves the cocoon, would be most effective in diminishing the nuisance, but poisoning is useful when resorted to in time.

J. F.

**Continuous Cropping with Wheat and Barley.** By A. VOELCKER (*Bied. Centr.*, 1881, 617—620).—This is a report of the fourth year of an experiment on the continued growth of wheat and barley in the same field, as carried out at Woburn for the Agricultural Society of England under the superintendence of Dr. Voelcker. The year 1880 was very unfavourable; heavy rains prevailed during the autumn, and the ears of wheat filled slowly and weighed light. The barley, however, prospered better, and apparently the ground was more suited to it than to the wheat. The following conclusions were drawn from the experiments:—

*Wheat*.—1. That in the soil of Woburn at least, and probably in similar light sandy soils, the growth of wheat continuously for a number of years cannot be carried on with profit, even when large quantities of the best artificial manures are employed. 2. Good and properly prepared stable manure had a very favourable effect on the crops as in preceding years. 3. Mineral manures, without nitrogen, had a better effect on the crop than nitrogenous manures without minerals. This was different in the preceding three years, during which the want of fixed plant-food was apparent. 4. The profitable working of a mixture of mineral and nitrogenous manures was, as formerly, very evident.

*Barley*.—1. Mineral manures alone without nitrogen had no effect on the crop. 2. Sodium nitrate alone had a better effect than ammoniacal salts without minerals; this is the reverse of former years. 3. Ammoniacal salts, together with mineral manures, produced more grain but less straw than the same quantity of minerals and sodium nitrate. 4. An increased quantity of ammoniacal salts with mineral manures had no better effect than the lesser quantity. 5, 6, 7. The stable manure had a very beneficial effect on the crops, and the doubling of the quantity had a greater. J. F.

**Experiments on Thin or Thick Seed-sowing.** By R. HEINRICH (*Bied. Centr.*, 1881, 620—623).—Many experiments have been made as to the advantages, or the reverse, of sowing seed thickly or thinly; they must all of them necessarily possess little more than a local interest, as the peculiarities of soil, climate, and manuring largely influence the results. The experiments in question were made with oats, in a poor sandy field, with a partial inclination towards the south. In 1879 three plots were sown with 5, 7·50, and 10 kilos. of oats; the yield was somewhat greater in the more thickly sown plots, but not in proportion to the seed sown, being only 5 : 6 : 7. The experiments were repeated in 1880 on a larger scale, with confirmatory results. The results summed up are:—Thick sowing produces a larger number of plants in a given space, but the plants are individually weaker. The quantity of stalk or halm produced varies very little in weight, whatever the quantity of seed employed on a given space of ground. A poor soil should be sown thinly. J. F.

**Modifications of Composition which Green Fodder undergoes when Preserved in Pits.** By G. LECHARTIER (*Compt. rend.*, 93, 734—737).—It has been previously shown that carbonic anhy-



dride, alcohol, and acetic acid are produced in the fermentation of green fodder.

In this paper analytical data are given. The fermentation experiments were conducted in flasks, in order that the samples examined before action and those taken after might be as much alike as possible. The maize fermented in the flask is exactly like that fermented in the pit, as far as composition is concerned:—

	Maize.		Clover.	
	Before fermentation.	Fermented.	Before fermentation.	Fermented.
Carbonic anhydride.....	—	2·180	—	1·42
Matter volatile at 100° ..	79·120	80·580	76·420	76·380
Alcohol.....	—	1·342	—	—
Nitrogenous matter.....	2·465	2·232	4·810	4·249
Ammonia.....	0·021	0·024	0·026	0·083
Glucose.....	2·064	0·143	0·474	0·452
Sugar.....	0·983	0·063	0·457	0·304
Starch.....	4·302	3·863	4·230	1·456
Pectous substances.....	0·344	0·178	1·303	0·501
Cellulose.....	6·337	5·939	8·015	7·191
Fatty matter.....	0·099	0·149	0·241	0·372
Total loss.....		4·077		5·136

In this way some of the nutritious principle is lost, but the residue is rendered more completely utilisable. Some experiments on the increase of fatty matter gave these results:—

	Before fermentation.	After fermentation.
Maize (as above) .....	0·57	0·91
Maize (put in pit) .....	0·62	1·84
Clover .....	2·01	3·05
Colza grain.....	239·80	245·30

The author thinks this may throw some light on the formation of fatty matters in the living plant. D. A. L.

**Exhaustion of Soils by Sodium Nitrate.** By EMMERLING and LOGES (*Bied. Centr.*, 1881, 583—585).—The practical and theoretical value of sodium nitrate as a manure is beyond doubt; but with this general acknowledgment of its value, practical men assert that its frequent employment exhausts the land and causes a reaction when a certain point is reached. The authors agree that such exhaustion is theoretically probable, and proceed to show by experiment that it is a fact. They attribute it, however, to the great increase of the crop produced by the sodium nitrate removing a large quantity of mineral constituents from the soil, which are not but should be replaced, and think that although the employment of the valuable manure for one

season is not exhausting, its frequent use should be accompanied by that of phosphatic and potash manures. J. F.

**Influence of Factory Waste-water and Gases on Vegetation and Soil.** By J. KÖNIG (*Bied. Centr.*, 1881, 577—579).—Agriculture has suffered much from the neighbourhood of certain factories without the subject having attracted sufficient attention. The author contributes some information on the subject. He gives the composition of some waste waters. Quantities are in milligrams per litre.

	From dyehouse.	Wire- drawers.	Sulphur ore washer.
Dry residue . . . . .	4476·2	7080·2	3306·2
Organic matter . . . . .	1345·5	—	—
Sulphuric acid . . . . .	1650·5	3198·8	1729·5
Oxide of iron . . . . .	—	2378·7	518·3
Alkaline chlorides . . . . .	—	93·4	92·6

Gas-water which has been boiled with milk of lime to extract ammonia showed the following on analysis:—

Dry residue . . . . .	20·4230
Cyanides with lime . . . . .	2·3282
Sulphate of calcium . . . . .	2·5633
Sulphite of calcium . . . . .	1·0913
Phenol compounds . . . . .	0·6080

The influence of sulphurous vapours on trees has long been a subject of remark. The author submitted the leaves and young shoots of different kinds of trees to analysis, selecting sickly and healthy specimens of each kind, and he found the sulphuric acid present in the sickly specimens to be greatly in excess of the others; the gas was given out by a zinc-smelting works.

The waste water from a zinc works containing zinc sulphate was found to be very injurious to the meadows on the banks which were irrigated with the water, their productiveness being very considerably diminished. The presence of zinc was clearly proved in the earth and in the grass grown on it. The author states that he has proved by experiment that the zinc acts injuriously by becoming fixed in the soil and freeing other bases, such as potash, lime, soda, magnesia, &c., letting them dissolve out. Waste water containing hydrochloric acid acts in a similar manner by rendering plant-foods unduly soluble and easily washed out of the soil. J. F.

**Agricultural Value of Leather Meal.** By A. PETERMANN (*Bied. Centr.*, 1881, 590—597).—The utilisation of a waste material so rich in nitrogen as leather, is important to the manure manufacturer and farmer. Considerable progress has been made in reducing the leather to fine powder by roasting and grinding, treating with superheated steam, &c., and the price of the nitrogen in such meal in Belgium is quoted at two-thirds that of nitrogen contained in ammonium sulphate and in sodium nitrate. The physical condition of the material leaves little to desire; its fine state of division allows contact with

the decomposing agents, and treatment with superheated steam removes the greater part of the tannic acid. Hitherto the agricultural value of leather meal has not been fairly tested, it being always sold mixed with other ingredients as a compound manure, and, as such, bought with readiness by farmers. In the absence of special information, the author undertook the experiments recorded in the present paper. They were of three kinds,—in the glasshouse with oats, in a garden with horse beans, and in the field with sugar-beets. In the glasshouse, blood meal and leather meal were tried against each other alone, and in mixtures of precipitated phosphates and chloride of potassium in various proportions. In all the experiments, it was found that the leather meal, whether alone or mixed with the phosphates and potash, did not produce an increase in the crop, but that the blood meal, combined with precipitated phosphates, caused an increase of double the produce of the unmanured. In the garden, with horse beans, the results were similar, the leather causing a scarcely perceptible increase, whilst sodium nitrate produced an increase of about 75 per cent. over the unmanured plots. The actual figures are in kilos. per hectare of beans:—

Unmanured.	Leather meal.	Sodium nitrate.
942·5	981·7	1695·8

The field experiments were of a more thorough nature, but were equally unfavourable to the leather. There were four sets of experiments—unmanured, phosphates only, leather meal with phosphates, and sodium nitrate with phosphates.

The tabulated results are instructive; the first column shows the total produce of beets per hectare, the second and third the increase in kilos. per hectare and per cent. over the average of the three unmanured plots:—

	Total produce. kilos.	Increase over average of total kilos. per cent.	
1. Unmanured .....	34,830	—	—
2. Superphosphate .....	34,380	510	= 1·5
3. Superphosphate and precipitated phosphate	34,290	420	= 1·2
4. Precipitated phosphate .....	34,380	510	= 1·5
5. Unmanured .....	33,840	—	—
6. Leather meal and soluble phosphate.	37,890	4020	= 11·9
7. Leather meal with soluble and pre- cipitated phosphate	37,480	3610	= 10·7
8. Leather meal and precipitated phos- phate	35,910	2040	= 6·0
9. Unmanured .....	32,940	—	—
10. Sodium nitrate and soluble phosphate	43,380	9510	= 28·1
11. Sodium nitrate with soluble and pre- cipitated phosphate	42,070	8200	= 24·2
12. Sodium nitrate with precipitated phosphate	43,830	9960	= 29·4

The latter manure produced by far the best results. In a financial point of view the results were:—Cost of manure per hectare: sodium nitrate, 128 francs; leather meal, 95 francs; phosphates, 45 francs. The loss by using leather meal and phosphates was 59 francs per hectare, and the gain by using sodium nitrate 58 francs as compared with the yield of unmanured parcels.

The experiments were made in sandy soil, and, of course, represent but one year's effects. The author invites cultivators to make similar and more extended experiments. J. F.

**Preservation of Stable Manure in Deep Stalls.** By HOLDEFLEISS and EMMERLING (*Bied. Centr.*, 1881, 586—588).—This paper records the results of allowing the manure to remain and accumulate under the cattle for a long period, in some instances for three months, in specially constructed deep stalls; in every case, as compared with the common practice of manure heaps, the manure so left was in more workable condition, the ammoniacal salts better preserved, and the proportion of all useful ingredients greater in comparison to the bulk.

Incidentally, the authors quote the value of nitrogen, potash, and phosphoric acid in stable manure at Marks 1.50—0.36, 0.40 per kilo. respectively. J. F.

**Peat as Litter.** By C. ARNOLD (*Bied. Centr.*, 1881, 589—590).—The use of peat ground to fine powder has been strongly recommended, and the experiments of Alberti show that it absorbs  $7\frac{1}{2}$  to 8 times its weight of water, whilst straw and sawdust only take up  $3\frac{1}{2}$  to 4 times their weight. In the present case a two-horse stable was laid down with 0.12 meter deep of ground peat; after six days there was no perceptible ammoniacal smell; a second stable containing two horses was bedded with straw. The air in both stables was daily tested for ammonia, the result being that the latter stable at the end of six days contained as much ammonia as the former at the end of 15 days. On the 20th day, the peat becoming damp, half the former quantity was added, when the ammonia in the air became very much reduced. One bale, weighing 128 kilos., costing 5 marks, lasted 30 days, 150 kilos. of straw, value  $7\frac{1}{2}$  marks, being used in the other stable; the absorptive power of the peat is regular, and is perceived, whether a large quantity is employed at once or the same quantity in three or four operations; the most economical method is to apply thin layers every six days. The author considers the material very suitable and economical, both in point of cost and space—the manure of two horses for a year occupying only the space of 20 cubic metres. J. F.

**Oats Manured with Steamed and Dissolved Bones.** By A. EMMERLING (*Bied. Centr.*, 1881, 597—599).—Continuation of previous experiments in the same direction made on clayey, humous, and sandy soils with bone meal steamed and with bone meal dissolved.

The results confirm previous experiences in favour of the dissolved bone, and show marked increased production in each case wherein the manure was used. The experiments take account only of the pro-

duce of the first year; the effects in the succeeding year, the author believes, would be found much greater. J. F.

**Solubility of Phosphates in Soil by Acids contained in the Roots of Plants.** By H. v. LIEBIG (*Bied. Centr.*, 1881, 579—582).—From numerous experiments, the author concludes that oxalic acid is the first acid formed in plants, being a step towards the production of hydrocarbons, but he believes that it also acts as a solvent of the phosphates contained in the soil. The albumin and hydrocarbons in seeds are sufficient with the potash and phosphoric acid present to provide rootlets and first leaflets. With the production of these and the absorption of carbonic acid, the formation of oxalic acid commences, and its combination with potash in the plant. When it comes into contact with the phosphoric acid in the soil, potassium phosphate is formed in the plant and calcium oxalate in the soil. As a support to this hypothesis, the author instances the success even in sterile soils of certain plants containing abundant oxalic acid. Lupines for example contain such a reserve of material that they can without the aid of external nourishment, develop a strong system of roots which act so energetically as to utilise the most refractory ingredients in the soil—if the assimilation of phosphates were due to the presence of water containing carbonic acid, those dry sterile soils would be absolutely unproductive.

Hitherto the method of estimating phosphates by their solubility in water, and of retrograde or precipitated phosphates by ammonium citrate, has not produced satisfactory results, and the author believes that the true test of the value of a phosphate is its solubility in such acids as are found in the roots of plants. He gives the results of some of his experiments.

In dilute acetic acid for 25 minutes was dissolved, of

Ground phosphorite containing 28 p. c. — 9·5 p. c. }	Phosphoric acid.
Baker guano „ 34 „ „ 11·5 „ }	
Mejillones guano „ 36 „ „ 14·6 „ }	

An additional quantity of acid dissolved more phosphate, but the amount is not stated.

Boiled for 25 minutes with 1 gram of calcium phosphate,  $1\frac{1}{2}$  gram potassium oxalate and 100 c.c. water dissolved—

Phosphorite .....	57·1	per cent. phosphoric acid.
Baker guano .....	71·0	„ „
Bone ash (meal) .....	50·4	„ „
Do. finely ground....	89·5	„ „

The same reagent in the cold worked more slowly, but in a similar way thus after 36 hours, dissolved, of—

Mejillones guano .....	74·6	per cent. phosphoric acid.
Steamed bone meal, fine ..	87·33	„ „
Do. do. coarse	51·7	„ „
Peruvian guano.....	95·4	„ „
Calcium biphosphate.....	100·0	„ „

Dr. Wein found only 53 per cent. of this calcium biphosphate soluble in ammonium citrate.

The author believes that these experiments, showing the different degrees of solubility in vegetable acids, or in other words, of power of assimilation by roots, are of considerable value, and that this mode of estimating the economic value of phosphates is preferable to field experiments, and that the name of "plant" or "root solubility" would be preferable to present terms.

Incidentally he shows the inutility of dissolving Peruvian guano, as far as phosphates are concerned, and mentions his belief that too much value has hitherto been attached to bone meals, much of their good effects being due to the nitrogen they contain: the fineness of the powdered bone he considers a valuable measure of its worth as a phosphatic manure.

J. F.

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## Analytical Chemistry.

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**New Method for Detecting the Evolution of Oxygen by Vegetable or Animal Organisms.** By T. W. ENGELMANN (*Biol. Centr.*, 1881, 629—630).—The method is based on the urgent requirement of oxygen by the bacteria of putrefaction, especially the more minute kinds. A drop of liquid rich with them is placed on the slide of a microscope, and the chlorophyll cells of certain plants introduced. The whole being well illuminated, the bacteria are seen crowded around the green cells, whilst the remainder of the drop contains no bacteria; on the light being turned down so that the object is barely visible, they disperse and are scattered over the entire drop. The author, from observations made in this manner, finds that plants containing chlorophyll give out oxygen energetically in the light; the energy of emission is in proportion to the chlorophyll contents of the cells; partially destroyed cells emit oxygen from their sound portions. The action of light in the process is local; a cell partially illuminated emits oxygen from that part only. Light of different wave-lengths varies in energy. The ultra-red is generally inactive. Orange and yellow stronger. Green nearly always weak. Blue is active. The action of light is instantaneous, the emission of the oxygen commencing at the very moment of illumination. J. F.

**Accurate and Rapid Method for Analysis of Air.** By E. W. MORLEY (*Am. Chem. J.* [3], 275—279; *Chem. News*, 44, 291—292).—The air is collected in stoppered bottles containing a few drops of potash, with which the stoppers are moistened, and in such a condition samples may be kept for many days without alteration.

The air is withdrawn from the bottle by means of a mercury pump connected with it by an india-rubber bung (in presence of an alkaline solution the bung does not absorb 0.001 per cent. of oxygen) and discharged into a jar standing over mercury. A portion of the air, sufficient to occupy 470—475 mm., is then introduced into a eudio-

meter, roughly measured with a journeyman pressure tube, and finally with an accurate pressure tube fitted with a Jolly point in the vacuum at the level of the zero of the graduation on the eudiometer tube, which zero is at the top of the tube. When the mercury in the pressure tube is put in contact with that in the eudiometer, and its lower level brought to the Jolly point by means of a fine adjustment, the level of the mercury is read by means of a microscope magnifying to 50 diameters. By such an arrangement the contact at the Jolly point can be verified, the thermometer read to 0.01 of a degree, and the level of the mercury in the eudiometer, in less than 10 seconds.

The measured quantity of air is then transferred to a jar and mixed with 63 per cent. of hydrogen. By always using this proportion of hydrogen, the error, which is a function of the hydrogen, remains constant. When the gases have had time to mix, the whole volume is transferred to the eudiometer and exploded.

To ensure accurate determinations of temperature, the whole apparatus is encased in a box, which is filled with water constantly agitated by a current of air.

The hydrogen used is prepared from a Bunsen's decomposing cell so constructed that it can be attached to an air-pump, and all hydrogen, either dissolved in the acid or occluded by the zinc, may be expelled before using it; the hydrogen is also passed over platinum-black; prepared in this way the gas may be kept over mercury for several weeks.

By making the corresponding readings of different experiments under similar circumstances, all errors disappear from the *differences* of the analyses. By this method analyses can be made with the greatest accuracy in 70 minutes.

L. T. O'S.

**Estimation of Potash in Wine.** By R. KAYSER (*Chem. Centr.*, 1881, 706).—In order to determine the potash in wine, the author proceeds as follows:—To 100 c.c. wine (clarified by charcoal) are added 7 grams hydrated sodium carbonate, and 2 grams tartaric acid, and finally 150 c.c. of alcohol of 92 per cent. The mixture is then allowed to stand for 24 hours in order to separate the potash as potassium hydrogen tartrate; this is thrown on a filter, washed with alcohol, and then dissolved in water in the vessel used for the wine. The solution is then made up to a known volume and titrated with a decinormal soda solution.

V. H. V.

**Analysis of Rail Steel.** By M. TROILIUS (*Chem. News*, 44, 299—300, and 310—311).—In the estimation of phosphorus in rail steel, the author advocates its determination as ammonium phosphomolybdate, weighing it as such without ignition. The weight of steel used is 5 grams, which is dissolved in aqua regia, the silica separated in the ordinary way, and the phosphorus precipitated in a nitric acid solution with ammonium molybdate prepared by dissolving 100 grams ammonium molybdate in 1 litre of water, and 100 c.c. ammonia, sp. gr. 0.88. The precipitate is filtered off after standing for an hour at a gentle heat. The precipitate is dried between 95° and 140°, detached from the filter-paper and weighed.



The precautions to be observed are—

- (1.) Removing excess of hydrochloric acid by evaporation.
- (2.) Adding the solution of molybdate in a thin stream from a pipette and shaking well.
- (3.) Great care in washing the precipitate, and brushing it off the filter-paper.

When the steel contains large quantities of arsenic, the temperature of the solution after adding the molybdate must not exceed  $40^{\circ}$ , otherwise the arsenic is precipitated.

In the method of burning the filter-paper, it is not necessary to make any allowance for ammonia expelled, if the filter-paper is carefully incinerated.

Since the above methods furnish sufficiently accurate results, the magnesia methods are considered a waste of time, and the results are frequently too high, owing to difficulty of obtaining the reagents used in them free from phosphorus.

*Determination of Silicon.*—The author advocates more especially the sulphuric acid method, and for each gram of steel uses 14 c.c. of dilute sulphuric acid (1—6), boils the mixture (with exclusion of air as far as possible) until the steel is completely dissolved, evaporates, dilutes the residue with hot water and a few drops of hydrochloric acid, and filters from the insoluble silica, which is washed with water containing 5 per cent. nitric acid.

The separation of the silica by aqua regia, as in the phosphorus determination, may be used.

*Manganese Determination.*—For the determination of manganese, the author uses the ammonium acetate and bromine method, with final addition of ammonia. 3 grams of steel are dissolved in aqua regia, the solution evaporated to dryness, dissolved in boiling hydrochloric acid, the volume made up to 750 c.c. with water, and the solution neutralised with ammonia or ammonium carbonate (excess of alkali must be avoided, otherwise the manganese will be precipitated); 20 to 30 c.c. of concentrated ammonium acetate are then added, the solution boiled, and the precipitate allowed to settle: if it will not settle, a few drops of ammonia (0.88) are cautiously added, and the solution again boiled. Care must be taken not to add too much ammonia, as the manganese may be precipitated. The precipitate is then filtered, dissolved in hydrochloric acid, the iron again precipitated as before and filtered, this filtrate being added to the first. In ordinary cases one washing is sufficient, but for spiegeleisen and ferromanganese it is desirable to redissolve the precipitate twice. After cooling, the manganese in the filtrate is oxidised with excess of bromine and precipitated with ammonia.

It is necessary that the solution be cold before oxidation, otherwise a violent evolution of nitrogen takes place, and the manganese remains in solution. Insufficient bromine also causes only partial precipitation.  
L. T. O'S.

**Method for Determination of Carbon in Steel.** By M. TROILIUS (*Chem. News*, 44, 292—294).—The author employs a somewhat modified form of Eggertz's method: 0.2 gram of the steel and of

standard steel are dissolved at 90° in nitric acid, which is delivered from a burette; when the steel is completely dissolved, and the solution quite cold, the determination is carried out in the carbon tubes. The following points are of much importance:—(1) the quantity of acid required for each 0.1 gram of steels of different percentages of carbon; (2) the minimum addition of water required for each 0.1 gram steel to remove the iron colour.

It is also desirable that the standard steel should have a percentage of carbon not differing very widely from that of the sample to be tested.

L. T. O'S.

**Determination of Phosphorus in Iron and Steel.** By E. AGTHE (*Dingl. polyt. J.*, **242**, 133—136).—Referring to the estimation of phosphorus in iron by precipitation with molybdic acid and subsequent precipitation with magnesia mixture, the author states that four hours' standing is more than sufficient to complete the precipitation of the phosphorus by molybdic acid. Nitric acid when present in too concentrated a form or too large a quantity, prevents the precipitation. Carbon must be destroyed completely, otherwise the results are too low. They are too high when the silicon in steel, white cast-iron, or ferromanganese (*i.e.*, iron with only small quantities of silicon) is not eliminated.

In conclusion, the author details the process which he adopts. The precipitants used are prepared as follows:—

115 grams of molybdic acid are dissolved in 460 grams of ammonia, sp. gr. = 0.96, and 1 litre of water is added. The mixture is then poured into 1 litre of nitric acid, sp. gr. = 1.2, allowed to stand for one day and finally filtered. The magnesia mixture is prepared by taking 101.5 grams magnesium chloride and 200 grams ammonium chloride, and adding 400 grams ammonia, sp. gr. 0.96, and 1 litre of water.

D. B.

**Estimation of Zinc in its Ores.** (*Dingl. polyt. J.*, **242**, 310).—Schneider recommends that the ore be dissolved in concentrated sulphuric acid and a small quantity of nitric acid. The solution of zinc sulphate is evaporated until 1 litre contains 2 grams of zinc. Sulphuretted hydrogen is then passed through the solution, which is said to precipitate the zinc completely (only 2 mgrms. of zinc per litre remain in solution).

D. B.

**Determination of Mercury.** (*Dingl. polyt. J.*, **242**, 302—304).—Eschka's method of estimating mercury (*ibid.*, **239**, 300) by means of metallic iron and amalgamation of gold presented difficulties in the commencement, consisting in the necessity of washing the amalgam with alcohol when bituminous samples were examined, and the formation of a fluid amalgam on the gold capsule, when rich ores were tested. These difficulties have recently been surmounted. Teuber proposes to add an oxidising agent, preferably red lead; to the bitumen, the washing with alcohol is then unnecessary, and any loss of amalgam is avoided. With highly bituminous substances, the amalgam is washed with ether, and red lead is used instead of iron filings to cover

the mass. The formation of a liquid amalgam is prevented by operating on a small quantity of substance. D. B.

**Qualitative and Quantitative Determination of Fusel Oil in Alcohol.** By H. HAGER (*Chem. Centr.*, 1881, 712—714).—In order to detect the presence of fusel oil, a rolled filter-paper is dipped into the alcohol to be examined; on allowing the moistened paper to dry at a temperature not exceeding 25°, the alcohol evaporates, leaving the fusel oil, which reveals itself by its characteristic smell. This test is more delicate if one-tenth of its volume of pure glycerol is added to the dilute alcohol. If only traces of the fusel oil are present, the roll of filter-paper is placed in a cylindrical tube open at both ends; the lower end is closed with the finger, and the test mixture of alcohol, water, and glycerol poured in to thoroughly moisten the paper. In the course of 24 hours the smell of the fusel oil is easily recognised, and remains permanent for more than a week. If ethereal oils are present, the mixture is distilled at the heat of the water-bath, and the residue mixed with an equal volume of water and filtered; only traces of the oil pass through the filter, and the method described above can then be used.

*Quantitative Determinations.*—Owing to the difference of vapour-tension of ethyl and amyl alcohols, the two liquids may easily be separated by fractional distillation without addition of glycerol. Experiments are quoted to show the accuracy of the process. If the spirit contains less than 70 per cent. alcohol, both water and fusel oil remain in the residue left on distillation; ether is then added, while the distillation is proceeding; and the ethereal solution is redistilled at 60°. If an ethereal oil is present, a few c.c. of glycerol are added, the distillation residue allowed to stand for a day, and then filtered to remove the oil. Another method of separating the ethereal oil from the glycerol and spirit consists in adding a little solid paraffin or wax to the liquid; the vessel containing it is then warmed to melt the wax, which runs down and takes up the ethereal oil; it is then allowed to solidify and is removed by filtration; the mixture is finally separated by distillation as above. V. H. V.

**Quantitative Estimation of Phenol.** By F. SALOMON (*Chem. Centr.*, 1881, 712).—For the estimation of phenol, the author uses the intimate mixture of sodium bromide and bromate obtained by the saturation of soda with bromine, and subsequent evaporation. On adding hydrochloric acid, bromine is set free, which reacts in the so-called nascent state on the phenol solution to be examined.

V. H. V.

**Analysis of Starch.** By F. SALOMON (*Chem. Centr.*, 1881, 712).—The author determines (I) the dried substance, (II) the ash, (III) the portions insoluble in dilute acids (cellulose, nitrogenous substances), and finally the starch by conversion with dilute hydrochloric acid into sugar, which is determined quantitatively.

V. H. V.

**Action of Different Kinds of Benzoic Acid and their Sodium Salts on Potassium Permanganate.** By C. SCHACHT (*Pharm. J.*

*Trans.*, **12**, 517—518).—Of the different preparations of benzoic acid, all with the exception of those prepared by sublimation and from Siam benzoïn in the moist way, which decolorise potassium permanganate solution, change the colour of the solution to green both in alkaline and acid solutions. The sodium salts of the different preparations of the acid act in a similar manner.

From experiments on the commercial sublimed acid, it appears to consist of the acid from toluene or urine sublimed with a small quantity of gum benzoïn to impart the smell of the gum to it. L. T. O'S.

**Identification of Alkaloids.** By E. CZUMPELITZ (*Chem. Centr.*, 1881, 710).—The author, starting with the idea that the colour reactions of alkaloids arise from a removal of water, has examined the action of zinc chloride on them. The substance to be examined is moistened with a few drops of zinc chloride solution (1 gram  $\text{ZnCl}_2$ , 30 c.c.  $\text{HCl}$ , 30 c.c.  $\text{H}_2\text{O}$ ), and then re-dried on a water-bath. The following alkaloids give under these conditions a colour reaction: strychnine, a rose-red; thebaine, gold; narceïne, olive-green; delphinine, red-brown; berberine, gold; veratrine, red; quinine, pale gold; digitaline, chestnut-brown; salicin, red-violet; santonin, blue-violet; cubebine, carmine-red. By this process the presence of salicin can easily be recognised in quinine. V. H. V.

**New Colour Reactions of Morphine, Codeine, and Atropine.** By D. VITALI (*Pharm. J. Trans.* [3], **12**, 459—460).—Tattersall found that by treating morphine in the cold with a very little sodium arsenate and some concentrated sulphuric acid, a violet coloration is produced, passing into light-green on heating. According to the author, the above reaction occurs but slowly in the cold, but on agitating with a glass rod, a bluish-red tint verging on violet is produced, passing, on continuing to heat, to dark-green, dirty greenish-blue, and finally light-green [ $\alpha$ ]. On cautiously adding water, the colour changes first to dark-red and then becomes decidedly blue; if, however, alcohol is added, the first drops produce a wine-red, a larger quantity a most magnificent violet. On adding acetic acid to the solution [ $\alpha$ ], it becomes wine-red; on further adding a few drops of ammonia solution, so as to leave the liquid still acid, a magnificent blue is developed, passing into an intense green on adding ammonia in excess. In like manner, the solution which has become blue by water, and that which has become violet by alcohol, are turned green by ammonia. The colouring matter remains suspended as a flocculent precipitate.

Morphine heated with sulphuric acid becomes first dark-red and then dark-green. Water, alcohol, acetic acid, and ammonia produce the same reactions as above, but the tints are not so vivid.

On dissolving a crystal of morphine in a few drops of sulphuric acid, adding a drop of sodium sulphide and cautiously heating, it turns to flesh-colour, changing to intense violet, dark-green, and dirty green. On adding a drop of sodium sulphide to morphine dissolved in two drops of sulphuric acid, then one drop of a 2 per cent. solution

of potassium chlorate in concentrated sulphuric acid, and stirring, a greenish tint is developed at first, turning to blue with a tendency to violet. With an additional drop, the green becomes intense and passes, with continued stirring, into dark blue; more of the chlorate solution produces a yellowish tint.

Codeine gives the same reactions, except that whilst morphine with sulphuric acid and sodium arsenate turns dirty green on heating, codeine treated in a similar manner assumes a fine reddish-violet tint, changing to green on further heating, and yielding the same colour reactions as morphine, with water, alcohol, &c.

If a solid fragment of atropine or one of its salts is moistened with a few drops of potassium chlorate in sulphuric acid, the former becomes greenish-blue, and on moving the liquid about in all directions, bluish-green streaks are seen to pass from the fragments through the liquid, the latter gradually assuming a pale-green colour. The colour reactions given by the author for atropine and daturine (*New Remedies*, 1880, 339) are likewise characteristic for hyoscyamine and duboisine.

F. L. T.

**Estimation of Quinine as Herapathite.** By A. CHRISTENSEN (*Pharm. J. Trans.* [3], 12, 441).—The method for estimating quinine as iodosulphate was first proposed by De Vrij; the author has re-examined it, and comes to the conclusion that (1) acidulated spirit dissolves a notable quantity of herapathite, too much and too little acid are alike disadvantageous; (2) the degree of concentration may affect the result; (3) cinchonidine periodosulphate may be precipitated in spite of De Vrij's precautions; (4) compounds of quinine richer than herapathite in iodine are formed unless the solutions are cold and the filtration takes place one hour (instead of 24, De Vrij) after precipitation. To avoid the formation of cinchonidine iodosulphate, the author proposes to separate the quinine by ether before precipitation.

F. L. T.

**Detection of Oleomargarin.** By P. CASAMAJOR (*Chem. News*, 44, 309—310).—This method consists in determining alcohol of the same sp. gr. as the suspected sample of butter.

Pure butter at 15° has the same sp. gr. as alcohol of 53·7 per cent., sp. gr. = 0·926, and oleomargarin as alcohol of 59·2 per cent., sp. gr. = 0·915. Any butter therefore which is adulterated with oleomargarin will float in alcohol of 53·7 per cent. In alcohol 56·5 per cent. (mean of 53·7 and 59·2) pure butter when melted will sink and oleomargarin will float; the butter on solidifying rises to the surface owing to its expansion, but in alcohol of 59·2 per cent. butter will sink at all temperatures.

In order to determine the amount of oleomargarin in butter, determine the strength of alcohol of same sp. gr. as sample; let it = 57 per cent.; from it take the strength of alcohol of same sp. gr. as butter = 53·7; multiply the remainder by the reciprocal of the difference of the strengths of alcohol of same sp. gr. as oleomargarin and butter = 0·18: ∴ (57 - 53·7) 0·18 = 3·3 × 0·18 = 5·95 of oleomargarin.

L. T. O'S.

**Estimation of Neutral Fats, and Palmitic and Oleic Acids in Palm Oils and Autoclaved Materials.** By F. SEAR (*Chem. News*, **44**, 299).—Five grams of the substance is treated with 100—150 c.c. carbon bisulphide for three or four hours with occasional shaking. The mixture is then filtered into a tared flask, the residue washed with carbon bisulphide, the filtrate freed by carbon bisulphide by distillation at as low a temperature as possible, dried, and weighed.

The residue consisting of neutral fats and zinc oleate is saponified with alcoholic potash; the soap is decomposed with an acid, the mixture filtered, and the zinc precipitated from the hot solution with potassium carbonate and estimated as zinc oxide. The quantity of zinc oleate to which this corresponds is calculated, and subtracting this number from the weight of neutral fats and zinc oleate gives the weight of the former. By calculating the amount of oleic acid from the zinc oleate, adding it to the weight of neutral fats, and subtracting their sum from the weight of oil taken, the amount of palmitic acid is readily ascertained. L. T. O'S.

**Diagnosis of Blood Stains by Measurement of the Blood-corpuscles.** By H. STRUVE (*Chem. Centr.*, 1881, 710).—The author has re-examined the method suggested by Malinin and Schmidt for the diagnosis of blood stains, which consists in heating them with 30—35 per cent. potash solution and measuring the corpuscles, in order to determine from what source the blood has been drawn. He finds that this method is valueless, because the blood-corpuscles, after having been dried and then soaked with potash, do not attain their original size, and no conclusions of value can be drawn from their measurement.

V. H. V.

**Examination of Urine for Albumin.** By A. RAABE (*Chem. Centr.*, 1881, 709).—In order to test urine for albumin, a small quantity of crystallised trichloroacetic acid is added to 1 c.c. clear filtered urine, and the mixture left at rest. The acid dissolves at the bottom of the vessel, and at the juncture of the two layers of liquid there appears a well-defined cloudy ring. If large quantities of urates are present, the turbidity takes a longer time to form, and is spread throughout the whole liquid; on warming, the turbidity caused by the urates disappears, but this does not occur if albumin is present.

V. H. V.

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### Technical Chemistry.

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**Manufacture of Soda.** (*Dingl. polyt. J.*, **242**, 293—297.)—Wiggs recommends for rotary soda-ovens a generator constructed to allow air to ascend in the same, which becomes heated, and combines with the gases of the generator before they are introduced into the ovens, thus a more perfect combustion is said to be occasioned. Referring to

Pauli's process of desulphurising soda-liquors, Scheurer-Kestner mentions that the addition of manganese dioxide considerably facilitates the oxidation of sulphides, especially at a temperature of 75°. To separate silicic acid, aluminium oxide, and iron, Brünner treats soda-liquors with sodium nitrate or the oxides of zinc, lead, iron, or manganese.

Rammelsberg has investigated red and yellow crystals obtained from the soda-liquors of the Schönebeck Alkali Works. On recrystallising these, colourless octohedrons of the following composition were obtained:— $\text{NaF}, 2\text{Na}_3\text{RO}_4, 18\text{H}_2\text{O} (\text{R} = \text{P} + \text{U})$ . From a solution of sodium fluoride, vanadate, phosphate, and hydroxide, crystals resembling the above-described octohedrons were obtained. From raw soda-liquors, Rammelsberg obtained crystals which he recognised as gay-lussite,  $\text{Na}_2\text{CO}_3, \text{CaCO}_3, 5\text{H}_2\text{O}$ , the formation of this salt being the cause of the loss in soda experienced at the Schönebeck Works.

D. B.

**Devitrification.** By M. GRÖGER (*Dingl. polyt. J.*, **242**, 297—302).—The author in this investigation used devitrified bottle-glass from the glass works of Aussig in Austria. This consisted of crystalline radiating fibrous globular masses, attaining a diameter of 5 cm. with faint greenish-white coloration, and imbedded in the perfectly transparent glass of deep green colour. Having carefully separated the devitrified particles from the transparent mass, both were analysed with the following results:—

	Devitrified glass.	Transparent mass.	Difference.
$\text{SiO}_2$ .....	63.79	64.39	— 0.60
$\text{Al}_2\text{O}_3$ .....	7.73	7.42	+ 0.31
$\text{FeO}$ .....	1.39	1.39	+ 0.00
$\text{MnO}$ .....	2.49	2.47	+ 0.02
$\text{CaO}$ .....	13.38	12.81	+ 0.57
$\text{MgO}$ .....	0.61	0.73	— 0.12
$\text{Na}_2\text{O}$ .....	9.76	9.78	— 0.02
$\text{K}_2\text{O}$ .....	1.52	1.45	+ 0.07

The difference in the chemical composition of the two masses is therefore very small, and confirms Pelouze's results, who found that devitrified glass has the same composition as the glass from which it is prepared. Devitrified glass is harder than ordinary glass, and less fusible. The author found that devitrified glass is considerably attacked by hydrochloric acid, 2 grams losing 0.484 gram against 0.032 loss of 2 grams ordinary glass. The residue obtained on treating devitrified glass with hydrochloric acid amounts to 77 per cent. The soluble and insoluble portions gave on analysis—

	$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{MnO}$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{Na}_2\text{O}$ .	$\text{K}_2\text{O}$ .
Insoluble..	51.70	7.29	1.45	2.01	4.50	0.56	8.70	0.99
Soluble ..	11.90	0.25	0.26	0.06	8.84	0.30	0.81	0.08
Total ....	63.60	7.54	1.71	2.07	13.34	0.86	9.51	1.07

These numbers seem to show that hydrochloric acid dissolves large quantities of lime present in glass in the form of monosilicate, the



crystalline substance in glass consisting of this compound, which is imbedded in the amorphous vitreous mass.

In conclusion the author states that devitrification is not a mere molecular change, as supposed by Pelouze, but is dependent on a dissociation of the vitreous mass, the result being that calcium monosilicate crystallises out.

D. B.

**Du Puy's Direct Process for Making Iron from Ores, Tapcinder, Mill Furnace Slag, and Hammer Scale.** (*Dingl. polyt. J.*, **242**, 290—293.)—This process consists in heating ore or slag mixed with carbonaceous substances and flux in thin cases made of sheet-iron placed in reverberatory furnaces for three or four hours. After the reduction of the ferric oxide, several of the cases are hammered together, squeezed, and rolled into bars. The cases of sheet-iron, which are partly destroyed during the operation, are not removed. Charcoal was first used, but later on, ordinary reducing agents, such as coal, anthracite, or coal-dust, were employed. The iron and steel produced is said to compete with the best Swedish and American brands.

In order to make the process more economical, Du Puy succeeded in abandoning the use of the iron cases, and now forms the mixture of ore and slag into the shape of tubular rings resembling drain-pipes. They are 40 to 48 cm. long, 29 cm. in diameter, and 7 cm. in thickness, and are said to stand handling without breaking if properly prepared. A mixture of lime, alumina, pulverised ore, and coal is used, the proportions of each depending on the composition of the ore to be reduced.

D. B.

**Ferromanganese used in Puddling Fine-grained Iron** (*Dingl. polyt. J.*, **242**, 307).—A specimen of puddle-steel exhibited at the Düsseldorf Exhibition showed the following tensile strengths. It was puddled from pig-iron containing 1·6 per cent. phosphorus, with the addition of 1 to 4 per cent. ferromanganese containing 67 per cent. manganese.

	Without the addition of ferromanganese.	With addition of ferromanganese.			
		1 p. c.	2 p. c.	3 p. c.	4 p. c.
Strength, k./sq. mm.....	36·7	40·7	42·2	42·6	44·8
Expansion, per cent. ....	9·5	17·0	18·0	25·0	27·0
Contraction „ .....	23·2	23·3	30·4	38·3	43·6

In a series of experiments made by Voigt, pig-iron was puddled with the following additions of ferromanganese: 1·5, 3, 4·5, and 7·5 per cent. No additional effect was produced, and contrary to expectation Voigt was unable to trace any regular increase in the above coefficients (strength, expansion, and contraction).

D. B.

**Strength of Iron and Steel at Low Temperatures.** (*Dingl. polyt. J.*, **242**, 288—290.)—In reference to the diminution in strength which iron suffers at low temperatures, Gautier reports the following facts. According to Knut Styffe, the tenacity of iron and steel is not diminished at the lowest temperatures which were observed in Sweden on this occasion. Between  $+100^{\circ}$  and  $+200^{\circ}$  the tensile strength of steel remains constant; with soft iron, however, it increases. The elongation does not alter at very low temperatures; between  $+100^{\circ}$  and  $200^{\circ}$  it is not sensibly diminished in the case of steel, but considerably with iron. The limit of elasticity of iron and steel increases at a very low temperature; it diminishes when iron is heated to  $250^{\circ}$ . The modulus of elasticity of iron and steel increases with a decrease in temperature, and *vice versa*. However, the differences are but slight (only 0.0005 for one degree).

Sandberg has experimented with a number of English, French, and Belgian rails with a view of ascertaining their capability of resisting concussive force. At  $-13^{\circ}$  the resistance to concussion was one-third or one-fourth that at  $+29^{\circ}$ . In the summer, English rails were 20 per cent. stronger than French rails, and these again were 30 per cent. stronger than English rails during the winter.

Webster has made a large number of similar trials with iron, cast-iron, Bessemer steel, and malleable cast-iron, at temperatures varying between  $-15^{\circ}$  and  $+16^{\circ}$ , which show that the resistance to concussion (especially of cast-iron) is diminished considerably with a decrease in temperature. D. B.

**Desulphurising Pig-iron.** By A. ROLLET (*Dingl. polyt. J.*, **242**, 220).—The process is carried on in a cupola furnace, rotary puddling furnace, or in the Bessemer converter. When the former is used, the product is desulphurised iron, whilst in the case of the two last-named apparatus the desulphuration is combined with a partial “puddling” of the metal. After the end of the operation, the conversion of the pig-iron into steel or malleable iron can be effected in the same furnace. As a novelty, the author claims (1) the use of fluorspar to form a fluid basic slag, the pig-iron being fused at a high temperature in the cupola lined with a basic substance; (2) desulphuration of the pig-iron in a puddling furnace or a Bessemer converter, in the presence of a basic slag and lining, the sulphuretted slag formed being removed by the addition of charcoal before the carbonisation of the iron takes place. When pig-iron rich in silicon, carbon, or manganese is operated on, the addition of charcoal is not needed. D. B.

**Phosphorescent Blast-furnace Slag.** (*Dingl. polyt. J.*, **242**, 309.)—The slag used for the production of grey cast-iron at the Saynerhütte, after the end of the smelting process, differed in its external appearances and chemical composition from the slag ordinarily obtained at that place. The charge consisted of 80 parts Nassau red iron-ore and 20 parts Horhausen brown iron-ore with the addition of Lahn lime. On gradually cooling the slag after the smelting operation was finished, decomposition set in, accompanied by a peculiar luminous effect, which disappeared when the slag was perfectly cold. The following

is an analysis of the charge used, of the iron smelted, and of the slag remaining after smelting:—

Charge.		Grey cast-iron.		Phospho- rescent slag	
SiO <sub>2</sub>	= 14·288	Si	= 1·092	SiO <sub>2</sub>	= 38·715
CaO	= 24·334	Ca	= 0·734	CaO	= 45·452
MgO	= distinct traces	Mg	= traces	MgO	= 0·879
MnO <sub>2</sub>	= do.	Mn	= 0·277	MnO <sub>2</sub>	} = 15·049
Fe <sub>2</sub> O <sub>3</sub>	= 52·292	Fe	= 97·432	Fe <sub>2</sub> O <sub>3</sub>	
Al <sub>2</sub> O <sub>3</sub>	= 8·554	Al	= 0·000	Al <sub>2</sub> O <sub>3</sub>	
PO <sub>5</sub>	= 0·258	P	= 0·181	PO <sub>5</sub>	= 0·045
<hr/>		<hr/>		<hr/>	
99·726		99·716		100·140	
				D. B.	

**Extraction of Silver, Copper, and Lead.** (*Dingl. polyt. J.*, **242**, 211—220.)—Macay extracts silver, copper, and lead by heating the pulverised ores with a solution of 1 part cupric chloride and 0·2 part sodium chloride. The mixture assumes a pasty condition, and is ground in crushing mills with vertical runners—steam being injected into the mass simultaneously. If the ore contains silver sulphide, the following decomposition takes place:— $4\text{CuCl}_2 + \text{NaCl} + \text{Ag}_2\text{S} = \text{Cu}_2\text{Cl}_2 + 2\text{CuCl}_2 + \text{NaCl} + 2\text{AgCl} + \text{S}$ . The liquid is removed, the residue lixiviated with hot acid water, and, when all the copper has been extracted, the silver chloride is dissolved in sodium thiosulphate. The mixture is then boiled with sulphur. Thus silver sulphide is produced, and the sodium thiosulphate recovered for further use. The sulphide is boiled with a solution of cupric and sodium chlorides, the silver chloride washed and dissolved in a hot solution of common salt. The silver is then precipitated by iron, the ferric chloride being worked up for colcothar. Ores containing essentially copper pyrites and galena are treated in a similar manner.

In order to extract silver and lead from mixed ores, Lyte proposes to pulverise the roasted ores, and dissolve the copper and zinc present in the ores with a hot solution of hydrochloric acid (15 to 17 per cent.), most of the silver and lead remaining undissolved. The solution is treated in a second vessel with a further quantity of calcined ore, copper and zinc are again extracted, any silver or lead dissolved in the first operation being precipitated. The solution is neutralised with chalk, iron and aluminium oxides being precipitated. The copper in solution is then separated with zinc, and the solution of the latter treated with milk of lime for the recovery of the zinc. The residue containing the chlorides of silver and lead is treated with a hot solution of salt, most of the lead chloride separating on cooling. The solution of silver chloride and the remaining lead chloride is treated with zinc, which precipitates the silver and lead in the metallic state. The precipitate is added to a further quantity of salt solution until it contains from 2 to 4 per cent. of silver, when the argentiferous lead is cupelled.

Raimondi discusses the application of magistral in American amalgamation. The ore is intimately mixed with common salt, and then treated with magistral. The latter is converted into cupric chloride,

which chlorinates the silver and mercury simultaneously. The mercury is added two or three days after the treatment with magistral, to allow part of the silver to be converted into the chloride and dissolved in the salt solution: the result is cuprous chloride. On adding the mercury, the non-chlorinated silver forms an amalgam, the cupric chloride unattacked in the ore forms calomel and cuprous chloride, and this reduces the slightly attacked silver sulphide, acting simultaneously and in conjunction with the mercury galvanically on the silver chloride, its nascent silver forming an amalgam with the mercury.

On the amalgamation of silver ores, see Rammelsberg (this Journal, 1881, Trans., 374). D. B.

**Clarification of Must.** By D. v. KOETH (*Bied. Centr.*, 1881, 635).—In a previous communication, Weigelt recommended the clearing of must by strong sulphuring of the vessels, as adding materially to the clearness and stability of the wine made from it. The author cautions persons against the practice; the sulphuric acid which is formed from the sulphurous fumes greatly increases the acidity of the wine, imparts a sharp smell and taste, and is actually injurious to health. The sulphuring precipitates albumin, arrests fermentation, develops acetic acid, and causes various other changes. Riesling wine, which has been so clarified, loses half its value in a few years; this is the opinion both of dealers in that wine and also of chemists.

J. F.

**Possibility of Magenta Disappearing from Coloured Wines.** By J. NESSLER (*Bied. Centr.*, 1881, 634—635).—The experiments were made in consequence of certain legal proceedings, and resulted in showing that magenta does not precipitate itself, nor is it precipitated by tannin, but, in presence of a sufficient quantity of permanent bodies with large superficial attraction, the magenta is precipitated completely. The various conditions under which wine is stored in cellars cause change in the physical state of the wine which often induces this precipitation. It is possible that from the same cask, wine with and without magenta can be obtained, and different results obtained by chemists, especially when it has stood some time, the upper layer being free from it.

J. F.

**Examination of Distilled Waters.** By J. NESSLER (*Arch. Pharm.* [3], 19, 161—170).—It has been stated that the presence or absence of calcium salts or other mineral matters could be taken as proof of adulteration or genuineness, but the author points out that such matters occur in undoubtedly pure samples, being either carried over mechanically on distillation, or added in the water required to dilute the spirit to a marketable strength.

The aromatic bodies present are in too small quantity to be examined; they may, however, be concentrated either by placing one end of a long strip of filter-paper in the liquid to be examined, and leaving the rest of the paper exposed to the air, so that the alcohol may evaporate, or by pouring a small quantity of the sample over fused calcium chloride, which combines with the alcohol, rendering

the aroma stronger, or by evaporating off the alcohol at 60°, leaving the essences concentrated.

If genuine cherry-water is poured over guaiacum-wood, a deep blue coloration is in most cases produced. This depends on the simultaneous presence of copper and hydrocyanic acid in the cherry-water. If either be absent, the coloration will not be produced. The presence of the copper is due to the worm, &c., of the condensing apparatus, and the hydrocyanic acid is derived from the kernels of the fruit. In different samples of distilled waters, Barth found amounts of copper varying from zero up to 0.015 gram of cupric acetate per litre. Hydrocyanic acid was present in all the 29 samples of cherry-water examined, but was present in only two samples of plum-water, the other samples of spirits examined being free from hydrocyanic acid.

F. L. T.

**Butter from Sweet and Sour Cream.** By M. SCHMOEGER (*Bied. Centr.*, 1881, 703).—Sour cream yields a larger amount of butter than sweet cream, and in a less time; but the percentage of fat is lower, there being a larger amount of water and casein present.

E. W. P.

**Butter and Cheese.** By G. ROBERT and others (*Bied. Centr.*, 1881, 705—707).—According to Robert, hard water is preferable for the washing of butter, as being more likely to remove any acids present. Neufchâtel cheese is prepared from milk, to which 6 per cent. of cream has been added, whilst Gruyère is prepared by kneading the curd from sweet milk in cream. The Norwegian cheese, Gammel-ost, is obtained by boiling sour milk, pressing the curd in a bag, and while there, again boiling it in whey, which gives the cheese its peculiar taste. When the curd has hardened, it is softened in water, to which has been added some juniper, and then packed in straw moistened with whey or cognac, &c. Saxon sour milk cheese is mixed with salt and caraway seeds.

E. W. P.

**Method of Freeing Maize from Fat before Employing it for the Manufacture of Spirit.** By M. C. LEEUW (*Bied. Centr.*, 1881, 702).—The fat present in maize is found to be objectionable when employing it for the manufacture of spirit; therefore to remove as much of the fat as possible, the maize is coarsely ground, and then thrown into a solution of common salt of sp. gr. 1.116, when the portion poor in fat sinks. By this process, 600 kilos. maize have been obtained containing 9 kilos. less of fat, and 15 kilos. more of starch, than would have been the case if the pure grain had been employed.

E. W. P.

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## General and Physical Chemistry.

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**Spectroscopic Investigations.** By G. L. CIAMICIAN (*Monatsh. Chem.*, 1, 631—633).—A continuation of the author's researches (*Abstr.*, 1879, 685; 1880, 361). The principal conclusions drawn by the author from a comparison of the spectra of related elements are the following:—Carbon has only two spectra, one of the first and one of the second order. The only carbon compounds possessing spectra peculiar to themselves are cyanogen, carbonic oxide, and acetylene. The spectra of cyanogen and of carbonic oxide, stand in simple relation to the spectra of the first order of their components.

The spectra of the second order, of carbon, boron, sulphur, and aluminium are homologous; these elements have also spectra of the first order which correspond. The spectra of both first and second order of carbon and magnesium are completely homologous. The spectra of barium, strontium, calcium, and magnesium are homologous at the more refractive end. The spectra of oxygen, sulphur, selenium, and tellurium are completely homologous. The spectra of phosphorus, arsenic, and antimony agree in the red with the nitrogen spectrum, and only the more refracted portion of the spectra of the halogens are homologous with that of fluorine. The less refracted sides of the spectra of silicon, aluminium, calcium, strontium, and barium are homologous with those of the spectra of the elements of the oxygen group, the resemblance being most marked on comparing those elements which form a horizontal series in Mendelejeff's table. The spectra of chlorine, bromine, iodine, phosphorus, arsenic, and antimony are homologous with those of the oxygen group on the more refracted side. From these resemblances, the author advances theories as to the compound nature of certain of the elements. Full details of the measurements of the spectra are given in the paper.

A. J. G.

**Spectra of Certain Alkaloids and Glucosides.** By C. HOCK (*Compt. rend.*, 93, 849—851).—The paper describes the characteristic absorption spectra of certain solutions of digitaline, dephinine, and belladonna. The layer of liquid used was about 5 mm. in thickness, and contained but a very small quantity of this substance.

R. R.

**Influence of the Structure of Organic Substances on their Refractive Power.** By KANONNIKOFF (*Bull. Soc. Chim.* [2], 36, 557—558).—The author has obtained the following results, the values of  $\frac{n-1}{d}$  and  $p\frac{n-1}{d}$  (molecular refractive energy) being calculated for a ray of infinite wave-length:—

	$\frac{n-1}{d}$	$p\frac{n-1}{d}$
Ethylene chloride .....	0·3441	34·06
Ethylidene chloride .....	0·3445	34·10
Monochlorethylene chloride ..	0·3166	42·26
Monochlorethylidene chloride .	0·3146	42·00
Dichlorethylene chloride ....	0·3012	50·60
Dichlorethylidene chloride ..	0·3019	50·72
Pentachlorethane .....	0·2916	59·05

Determinations with the alcohols of the  $C_nH_{2n-1}OH$  series, containing one double bond, and the  $C_nH_{2n-3}OH$  series containing two double bonds, confirm Brühl's law that the molecular refractive energy is greater than the calculated value by 2 units for each double bond between the carbon-atoms.

		$p\frac{n-1}{d}$ .	Calc.	Difference.
$C_nH_{2n-1}OH$ {	Allyl-dimethyl carbinol . . . .	49·8	47·5	+ 2·3
	Allyl-diethyl carbinol . . . . .	64·4	62·2	+ 2·2
	Allyl-methyl propyl carbinol	65·1	62·4	+ 2·7
	Allyl-dipropyl carbinol. . . . .	79·6	77·3	+ 2·3
$C_nH_{2n-3}OH$ {	Diallyl carbinol . . . . .	56·6	52·4	+ 4·2
	Diallyl-methyl carbinol . . . .	63·8	59·6	+ 4·2
	Diallyl-propyl carbinol. . . . .	78·7	74·5	+ 4·2

The establishment of a double bond between carbon-atoms is always accompanied by an increase in specific refractive energy equivalent to the diminution in specific refractive energy caused by the elimination of two atoms of hydrogen. This varies between 1 and 2 in the second decimal place. For example:—

	$\frac{n-1}{d}$	Difference.
Amyl alcohol, $C_5H_{12}O$ .....	0·4888	—
Valeral, $C_5H_{10}O$ .....	0·4728	— 0·0160
Allyl-ethyl ether, $C_5H_{10}O$ ....	0·4907	+ 0·0179

The following results were also obtained:—

	$p\frac{n-1}{d}$	Calc.	Diff.
Peppermint camphor, $C_{10}H_{20}O$ .....	77·6	77·1	+ 0·5
Cajeputene hydrate, $C_{10}H_{18}O$ .....	74·8	74·5	+ 0·3
Terebenthene hydrate (lævogyrate), $C_{10}H_{18}O$	77·1	74·5	+ 2·6
French terebenthene (lævogyrate), $C_{10}H_{18}$ ..	71·7	69·2	+ 2·5
Hydrocarbon from <i>Oleum Camille</i> .....	71·9	69·2	+ 2·7
Hydrocarbon from <i>Oleum Thymiani</i> .....	71·4	69·2	+ 2·2
Isoterebenthene .....	73·6	69·2	+ 4·4
Carvol, $C_{10}H_{14}O$ .....	74·8	69·4	+ 5·4
Cymene from camphor, $C_{10}H_{14}$ .....	72·0	66·6	+ 5·4

These values show that peppermint camphor and cajeputene hydrate have no double bonds; lævogyrate terebenthene hydrate,

lævogryate terebenthene from French essence, and the hydrocarbons *Ol. Camillæ* and *Ol. Thymiani* have one double bond; isoterebenthene has two, and carvol and cymene from camphor have three. This supposition is confirmed by comparing the molecular refractive energy of these substances with that of others of known constitution.

C. H. B.

**Determination of the Specific Refraction of Solid Bodies in Solution.** By P. P. BEDSON and W. C. WILLIAMS (*Ber.*, 14, 2549—2556).—In order to decide the disputed question whether it is possible to deduce the specific refraction of a solid body from the refractive power of its solution (of known strength), the authors determined the refractive power of polished prisms of rock salt, anhydrous borax and boric acid, and found that they agreed closely with the values obtained from solutions of these bodies, *e.g.*,

	<i>t.</i>	$\frac{A-1}{d}^*$
Rock-salt prism .....	15.0°	0.2426
Calculated from solution.....	20.0	0.2524
Borax prism .....	18.5	0.2120
Calculated from solution.....	20.0	0.2112
Boric acid prism .....	15.8	0.2444
Calculated from solution.....	20.0	0.2442
Sodium metaphosphate, solid..	20.0	0.1862
Sodium metaphosphate from solution .....	20.0	0.1885

The authors have also shown that the specific refraction of liquid phenol at 40° and 45° is identical with the values calculated from solutions of phenol in alcohol or in acetic acid.

The refractive index of a solid may be determined directly by immersing it in a liquid of greater refractive power, and then adding a feebly refractive liquid until the refractive power of the mixture appears to be the same as that of the solid suspended in it. The index of refraction of the mixture is then determined.

Determinations of the refractive power of rock salt, borax, and sodium metaphosphate gave satisfactory results by this method.

W. C. W.

**Relation between Molecular Refraction and Chemical Constitution.** By H. SCHRÖDER (*Ber.*, 14, 2513—2516).—The author finds that the *refraction-constitution* and the *volume-constitution* of saturated organic compounds are identical, and may be represented by the same formulæ, *e.g.*, for propionic acid the molecular volume is  $C_3H_6O_2 = 84 = 12 \times 7.0$ , and the molecular refraction is  $C_3H_6O_2 = 28 = 12 \times 2.33$  for A.

The atomic refraction of an element varies (within narrow limits) according to the element it is combined with. The stere of molecular refraction, as well as the molecular volume stere, increases slightly with the increasing molecular weight of the compound.

The volume and the refraction constitution are not identical in the case of non-saturated organic compounds. Thus the pair of carbon-

\* A = ray of infinite wave-length.



atoms united by double linking, in allyl, has the refraction constitution  $C_2^4$  and the volume constitution  $C_2^3$ , e.g.,

*Amylene*.—Molecular refraction,  $C_6^2H_{10}^{10} = 32.29 = 17 \times 2.31$  for A.

„ Molecular volume,  $C_5^6H_{10}^{10} = 111.4 = 16 \times 6.96$ .

In the aromatic compounds, the carbon-atoms of the benzene nucleus have the value  $C_6^{12}$  for refraction constitution, and  $C_6^8$  for volume constitution, e.g.,

*Toluene*.—Molecular refraction,  $C_6^{12}H_5^5.C_1^1H_3^3 = 50.06 = 21 \times 2.38$  for A.

„ Molecular volume,  $C_6^8H_5^5.C_1^1H_3^3 = 120.5 = 17 \times 7.09$ .

W. C. W.

**Action of Sunlight on Glass.** By T. GAFFIELD (*Dingl. polyt. J.*, **242**, 447—449).—The action of sunlight on glass was tried with a large number of different kinds of colourless and coloured glass, the changes of colour observed being from white to yellowish-white; green to yellowish-green; yellowish-brown and green to purple; greenish-white to blue; blue and other shades to correspondingly darker shades. From the results, which are discussed very fully in the original paper, several theories may be deduced. The colorations are attributable to the presence of ferric oxide, arsenic, charcoal, or sulphates in glass, but more especially to the presence of manganese used to decolorise glass.

D. B.

**Grove's, Planté's, and Faure's Secondary Batteries.** By W. G. ADAMS (*Chem. News*, **45**, 1—5).—An historical sketch and general account of secondary batteries.

**Electric Current Produced by Light.** By P. LAUR (*Compt. rend.*, **93**, 851).—A porous vessel filled with mercury and containing a strip of platinum is immersed in a solution containing sodium chloride and cupric sulphate, into which dips a plate of silver sulphide, which forms the other electrode, the circuit being completed through a galvanometer. When the apparatus is exposed to sunlight, the deflection indicates a current in which the silver sulphide acts as the negative pole. The movements of the needle of the galvanometer respond to variations of the luminous intensity, as when for example, a cloud passes over the sun. The explanation is that the cupric chloride formed by the mixture of sodium chloride and cupric sulphate, acts on the mercury; and the cuprous chloride then formed reduces the silver sulphide, but this reaction takes place only in the presence of the solar rays.

R. R.

**Reversibility of the Electro-Chemical Method for the Determination of Equipotential Systems.** By A. GUÉBHAUD (*Compt. rend.*, **93**, 792—794).—The paper describes the peculiar construction of electrodes by which the author has been enabled to apply his electro-chemical method to realise an idea enunciated by Töpler (*Pogg. Ann.*, **160**, 387) as to the possible reversibility and transformation of two systems, one into the other, of equipotentials and of discharge.

R. R.

**Researches on Electrolysis.** By BERTHELOT (*Compt. rend.*, **93**, 757—762).—The researches on the electrolysis of sulphates continued in this paper have reference to sulphates of metals forming more than one series of salts. The smallest electromotive force capable of effecting a decomposition of a solution of ferrous sulphate gives rise to a deposit of metallic iron on the negative pole; but there is no evolution of gas observed with 2 D. or less, the oxygen going to convert the ferrous into ferric sulphate. If the electromotive force is increased, oxygen and hydrogen appear at the poles, with formation of oxide and acid.

With manganous sulphate the minimum electromotive force causes a precipitate of manganese dioxide at the positive pole, while hydrogen is disengaged at the negative. If the electromotive force is increased, there comes a moment when the so-called normal action takes place; oxygen is disengaged, and manganese precipitated at the negative electrode.

In all cases, the thermic equivalents of the electromotive forces correspond with those required for the chemical actions. In the electrolysis of alkaline sulphates and nitrates, very complex reactions arise by reason of polarisation phenomena, which render the determination of the minimum efficacious electromotive forces uncertain.

R. R.

**Electrolysis of Water.** By D. TOMMASI (*Compt. rend.*, **93**, 790—792, and 846).—This paper, continuing a former one (*Compt. rend.*, 24th Oct., 1881), records the author's observations on the electrolytic action in the voltameter, produced by a single cell of zinc-copper or zinc-carbon and dilute sulphuric acid, when the voltameter electrodes are formed of certain metals or of certain pairs of different metals. The water is decomposed when the positive electrode is formed of a metal capable of directly combining with the oxygen of the water.

When water is decomposed by a single voltaic cell, a copper wire being used as positive electrode, and a platinum wire as negative electrode, the quantity of copper dissolved is greater than the quantity deposited upon the negative electrode. This may be explained by reference to thermochemical data.

R. R.

**Electrical Resistance of Vacuum.** By E. EDLUND (*Phil. Mag.* [5], **13**, 1—20).—This paper contains an historical account and theoretical discussion of the more important researches on this subject. The author concludes that the fact that electricity cannot penetrate an almost complete vacuum, depends on the resistance upon the electrodes continuing to increase with the continuation of the rarefaction, until it receives so great an augmentation that the current cannot circulate, and is not due to the specific resistance of the gas, or we should have to suppose this to decrease with the pressure only to a certain limit, and then to acquire a very high value, as the last molecules of gas are removed. From these observations it would appear that an *absolute vacuum is to be regarded as a conductor*. This is the only explanation which can be given of the fact that, without electrodes, a current can be called forth by induction, in a vacuum deprived of gas, whilst it is impossible for a current to pass there

between electrodes. It also removes the difficulty of explaining the electrical influence of one heavenly body on another. T. C.

**Electrical Resistance and Coefficient of Expansion of Incandescent Platinum.** By E. L. NICHOLS (*Phil. Mag.* [5], 13, 38—43).—The author concludes from his experiments that high temperatures may be determined with a much greater degree of exactitude from the expansion of platinum than from the increase in the resistance which the metal offers to an electric current, as in the method employed by Siemens in his resistance-pyrometer. The results given by the resistance-pyrometer are often quite fallacious, and not unfrequently differ by hundreds of degrees from the temperatures registered by the expansion-pyrometer. This is due to the fact that the formulæ employed for calculating the temperature from the resistance, are for the most part based on unwarrantable suppositions, such as the constancy of the specific heat of copper and platinum, the constancy of the coefficient of expansion of the latter metal, and on the accuracy of certain very doubtful values for the boiling points of zinc and cadmium. Further, owing to the varying resistance of different specimens of platinum, the formulæ for the calculation of temperature from the electric resistance, are applicable only for the identical wire for which the law of change of resistance with the temperature has been determined. From the available data, we are not in a position to calculate the temperature of an incandescent platinum wire from its change of resistance, or from its length, or, indeed, in any other manner, further than to express the temperature in terms of the length or the resistance of the wire. T. C.

**The Boiling Point of Antimony Iodide, and a New Form of Air Thermometer.** By J. P. COOKE (*Chem. News*, 44, 255—257).—The instrument consists of about 5 inches of thermometer tubing, 1 inch from the end it is cut, and 3 inches of half-inch glass tubing fused in, and the short end sealed. After being left in the vapour, &c., whose temperature is required, for a sufficient length of time, the long tube is sealed, and it is then removed to a mercury trough, the end broken under mercury, and so left to regain the temperature of the room. The height of the mercury column is then ascertained, the weight of the mercury and weight when quite full of mercury. From these data, the heights of the barometer, the temperature of the air, and the expansion of the glass used, the temperature sought can be found within an error of 1° C. Four determinations of the boiling point of sulphur differ in mean only  $\pm 0.3^\circ$  from the determinations of Regnault. Three determinations of the boiling point of antimony iodide gave, with the barometer at 758.1, 758.4, and 759.3 mm., the boiling point as 400.4°, 400.9°, and 400.9°; hence at 760 mm. it is 401.0 with  $\pm 0.5^\circ$ . The method is to be recommended for its simplicity and accuracy. A simple form of differential air thermometer is also described, which may be constructed for either lower or higher temperatures than that of the air; the indicator is a small mercury plug. The readings are as exact as those of a mercurial thermometer. H. B.

**Specific Heats and Latent Heats of Evaporation of Three Saturated Alcohols.** By D. I. DIAKONOFF (*Journal of the Russian Physico-chemical Society*, 1882, 2). The author obtained the following numbers :—

	Specific heat.	Latent heat of evaporation.
For normal propyl alcohol . . . . .	0·66972	165·92336
For amyl alcohol (by ferment.) ..	0·67902	123·78626
For dimethyl ethyl carbinol ....	0·76952	107·37988

Berthelot's methods were used for the determinations. The apparatus for determining the latent heat of evaporation has been modified by the author. B. B.

**Alleged Heating of Ice under Low Pressures.** By A. BUTLEROW (*Bull. Soc. Chim.* [2], 36, 307).—Butlerow has repeated Carnelley's experiment of heating ice under low pressure. He states that the ice evaporates gently without melting, but he has not succeeded in raising its temperature. In the apparatus employed, the thermometer was surrounded with a thin piece of platinum foil, and the space between it and the bulb was also filled with ice. The author considers that explanations offered by Lodge are scarcely admissible. If the ice becomes warm the interior should melt easily, as the change of state is accompanied by a diminution of volume. The temperature in the mass of ice ought to remain *below* the melting point, in the same manner that a liquid in a state of spheroidal ebullition has a temperature below its boiling point. The ice, in fact, further resembles it in evaporating only on the surface. The author thinks that the results of Carnelley's calorimeter experiments may perhaps be explained by the presence of a layer of vapour at a high temperature, which adheres to the ice as it falls into the calorimeter. J. I. W.

**Isomeric State of Haloid Salts.** By BERTHELOT (*Compt. rend.*, 93, 870—876).—The conversion of the yellow into the red modification of mercuric iodide is accompanied by an evolution of + 3 cal. for  $\text{HgI}_2$ . A former statement is repeated, that when silver iodide is first precipitated, it forms an unstable modification, which is gradually changed into a more stable form. When silver nitrate is added to potassium iodide, 26·9 cal. are evolved in the first two minutes, 21·1 cal. of which are evolved during the first half minute, whilst 6·6 cal. are more slowly evolved, and are dependent on the gradual change of the silver iodide from the less to the more stable form. Silver iodide also appears in the unstable form when it is separated from the double salt,  $\text{AgI} \cdot 3\text{KI} \cdot \frac{1}{2}\text{H}_2\text{O}$ , by the addition of water, as is proved by its immediate solubility in potassium cyanide. After standing some time the precipitate always gives the same amount of heat as the crystallised iodide of silver. A thermal difference between the stable, amorphous, and the crystalline forms of silver iodide cannot be detected; this remark also applied to the chloride, bromide, and cyanide of silver. The paper concludes with some general considerations bearing on the above. T. C.

**Heat of Combustion of Pinacone.** By W. LOUGUININE (*Bull. Soc. Chim.* [2], **36**, 307—310).—The author compares the heat of combustion of pinacone,  $\text{OH.CMe}_2.\text{CMe}_2.\text{OH}$ , with those of glycol and isopropylene glycol. It is necessary, however, to add the heat of fusion of pinacone to its heat of combustion to obtain a number exactly comparable with the others. The heat evolved by the combustion of a gram of pinacone was 7607.62 t.-u. The number of grams equivalent to a molecule would yield 897,699.16 t.-u. The corresponding number for glycol is 283,293 t.-u., and for isopropylene glycol 436,240 t.-u., giving a difference for  $\text{CH}_2$  of 152,947 t.-u. Calculating the heat of combustion of pinacone from these data, the number 895,081 t.-u. is obtained, which agrees closely with that obtained by experiment (897,699.16).

The heat of combustion of solid trimethyl carbinol (b. p.  $83^\circ$ ), the tertiary isomeride of butyl alcohol, has been determined by the author from two different samples. The heat evolved by a gram is 8551.56 t.-u. The number of grams equivalent to a molecule would yield 632,815.44 t.-u., to which must be added the heat of fusion. The author proposes to determine this at a later period.

The heat of combustion of liquid isobutyl alcohol,  $\text{CMe}_2\text{H.CH}_2.\text{OH}$ , is 636,706 t.-u. Favre and Silbermann found 633,440. The similarity of the heats of combustion of these two compounds is a further confirmation of the fact previously shown by the author, that isomeric bodies having the same chemical properties have identical heats of combustion. The fact is easily explained by the circumstance that in all the isomerides studied by the author the number and character of the atomic links are the same. Consequently, the energy which corresponds to the sum of these links in one of the isomerides, cannot differ from the energy of the other. The case is different when the isomerides have different chemical properties, different heats of combustion being observed. Thomsen (*Ber.*, **13**, 1388) has suggested that the isomerism of hydrocarbons results either from the different grouping of the carbon-atoms or from the manner in which they are connected.

J. I. W.

**Determination of the Volume Constitution of Bodies in the Solid State, when the Volume Constitution of the same Bodies in the Liquid State is known.** By H. SCHRÖDER (*Ber.*, **14**, 2516—2520).—The sp. gr. and molecular volume of the following substances in the solid state have been determined:—

	Sp. gr.	Mol. vol.
Diphenyl .....	1.165	132.2
Triphenyl benzene ..	1.205	253.8
Tetraphenylethane ..	1.182	282.8
Thymol .....	1.032	145.4

The volume constitution of these compounds is the same in the solid as in the liquid state; but the value of the stere is different. For the above substances in the solid state, the stere is equal to 5.04—5.11.

W. C. W.

**Artificial Production of Elementary Organic Forms.** By D. MONNIER and C. VOGT (*Compt. rend.*, **94**, 45—46).—Elementary forms presenting all the characters of organic elements,

such as simple cells, closed tubes, &c., may be artificially produced by the action of two salts, which produce one or two insoluble compounds in a liquid favourable to the formation of the pseudo-organic forms, one salt being dissolved in the liquid, the other being present in the solid state.

The pseudo-organic forms are produced equally well in liquids of wholly organic nature, semi-organic as sucrate of calcium, or inorganic as sodium silicate, and therefore the question of distinctive forms for inorganic bodies on the one hand and organic on the other disappears.

The formation of these elements depends on the nature, viscous constitution, and concentration of the liquids. They are not produced in certain viscous solutions, such as those of gum arabic or zinc chloride. The structure of the elements is related to the crystallised salts, and is as constant as the crystalline form of minerals; these forms are so marked as to serve to detect the most minute quantity of a substance in a mixture, and hence may be employed as a means for analysis. The structure is chiefly determined by the acid; thus phosphates and sulphates in certain cases give rise to tubes, whilst carbonates give cells. Copper, zinc, and nickel sulphates do not produce these pseudo-organic forms, and whilst calcium sucrate gives rise to this form, strontium sucrate does not.

These artificially produced forms are surrounded by true membranes dialysing in the highest degree, and containing heterogeneous substances, producing, in their interior, granulations disposed in a determinate order.

It is probable that inorganic elements contained in protoplasm play a certain part in the constitution of organic figured elements in determining their structure.

L. T. O'S.

**Diffusion of Solids.** By A. COLSON (*Compt. rend.*, **94**, 26—28).—Influence of time. *At any given temperature the coefficient of diffusion of carbon in iron is constant.*

This is true whether the iron already contains carbon or not; but is liable to exception at the conversion of steel into cast-iron.

The author's results show a seeming discrepancy—

	Weight before heating.	Weight after heating.
Disc A, already containing carbon..	6.982	6.992
Disc B, new .....	7.405	7.418

The difference between the increase in the weights of the two discs is 3 mgrms., but this is due to the oxidation of the iron in the case of B, consequent on the decomposition of the carbonic oxide, experiment showing that exactly that weight of oxygen (3 mgrms.) is absorbed. The disc A had already undergone this oxidation before heating; therefore by diminishing by 3 mgrms. the increase sustained by B identical results are obtained in each case.

Silica diffuses much more readily than carbon, as is seen by placing a platinum wire in the midst of lamp-black (free from silica) in a hessian crucible surrounded with a mixture of limestone and charcoal,

and heating in a furnace, when silicon is found in the platinum and diffused through the lamp-black as silica. If heated sufficiently long, the wire becomes crystalline, and has the composition  $\text{Pt}_2\text{Si}$ .

By using lamp-black containing 60 per cent. silica,  $\text{Pt}_3\text{Si}_2$  is obtained, a crystalline body (sp. gr. 14.1) melting at the same temperature as ordinary glass, which will not absorb a further quantity of silica.

By a similar method a silicide of iron (sp. gr. 6.6) containing 15 per cent. silicon may be obtained. It is formed even below  $1000^\circ$ .

Other metals yield similar compounds, and in all probability the property is possessed by other bodies. The method of formation is analogous to that by which Frémy has decomposed sulphides by water, in both cases chemical action taking place between a body in motion and a stationary body, which is either an oxide, a carbide, or a mixture of carbon and a metal.

L. T. O'S.

**Diffusion of Carbon.** By J. VIOLE (*Compt. rend.*, **94**, 28—29). —Referring to Colson's paper "On the Diffusion of Solids in Solids" (preceding Abstr.), the author records results observed by himself on the diffusion of carbon in porcelain during his research on the specific heat and heat of fusion of palladium (*ibid.*, **87**, 98). The palladium was heated in a porcelain crucible surrounded by plumbago, and placed in a plumbago crucible. After heating to  $1500^\circ$  the plumbago had transferred itself by diffusion to the porcelain crucible, which on the exterior presented the appearance of a plumbago crucible, whilst the plumbago crucible was like an earthen one.

The author has hitherto delayed publishing these results until he had had the opportunity of further studying the phenomenon.

L. T. O'S.

**Relation between the Atomic Weights of Elementary Bodies.** By FEDAROFF (*Bull. Soc. Chim.* [2], **36**, 559—560).

Group I.	Group II.	Group III.	Group IV.	Group V.
Li .. 4.5	Be .. 5.0	B .. 5.5	C .. 6.0	N .. 6.5
Na .. 9.0	Mg .. 9.5	Al .. 10.0	Si .. 10.5	P .. 11.0
K .. 12.5	Ca .. 13.0	? .. 13.5	Ti .. 14.0	V .. 14.5
Cu .. 17.0	Zn .. 17.5	Ga .. 18.0	? .. 18.5	As .. 19.0
Rb .. 20.5	Sr .. 21.0	? .. 21.5	Zr .. 22.0	Nb .. 22.5
Ag .. 25.0	Cd .. 25.5	In .. 26.0	In .. 26.5	Sb .. 27.0
Cs .. 28.5	Ba .. 29.0	? .. 29.5	? .. 30.0	? .. 30.5
? .. 32.5	? .. 33.0	? .. 33.5	? .. 34.0	Ta .. 34.5
Au } 37.0	Hg .. 37.5	Tl .. 38.0	Pb .. 38.5	Bi .. 39.0
Pt }	? .. 41.0	? .. 41.5	Th .. 42.0	? .. 42.5
? .. 40.5				

Group VI.		Group VII.		Group VIII.			
O ..	7.0	Fl ..	7.5	?	..	8.0	? .. 8.5
S ..	11.5	Cl ..	12.0		—		—
Cr ..	15.0	Mn ..	15.5	Fe ..	16.0	Ni }	16.5
Se ..	19.5	Br ..	20.0		—	CO }	—
Mo ..	23.0	? ..	23.5		—		—
Te ..	27.5	I ..	28.0	Ru }	24.0	Pd ..	24.5
? ..	31.0	? ..	31.5	Rh }	—		—
W ..	35.0	? ..	35.5		—		—
? ..	39.5	? ..	40.0	? ..	32.0		—
U ..	43.0	? ..	—	Os ..	36.0	Ir ..	36.5

To obtain approximately the atomic weights of the elements, it is simply necessary to raise the numbers in the table to the power  $\frac{3}{2}$ ,

and multiply the result by  $\frac{7}{8}$ . Admitting the homogeneity and simi-

larity of atoms, one must conclude that *the elements are arranged in the natural system in arithmetical progression increasing with the surfaces of their atoms*. In Group VIII, for example, the ratios of the atomic surfaces are 4, 6, and 9, whilst the surfaces of chlorine, bromine, and iodine are as 3, 5, and 7. The atomicity and general chemical properties of the elements are essential functions of these surfaces.  
C. H. B.

**Connection between the Atomic Weight and the Chemical and Physical Properties of Elements.** By T. BAYLEY (*Phil. Mag.* [5], 13, 26—37).—The elements are arranged in the order of their atomic weights, and are divided into series or periods and into groups, as in Mendelejeff's classification. The series are further grouped together in cycles in such a way that the first two cycles consist of Mendelejeff's first and second series respectively, the third cycle contains the fourth and fifth series, the fourth cycle the sixth and seventh series, and the fifth cycle the eighth, ninth, tenth, and eleventh series. It will be seen that all these cycles except the fifth correspond to Mendelejeff's short and long periods. The series, which in its early form is cyclic, loses its prominent features as the atomic weight progresses, whilst the cyclic change retains its characteristics unimpaired from the lowest to the highest known atomic weight.

The periodic changes which the physical properties of the elements undergo are traced in several cases, of which the following are more especially worthy of notice as not having been previously observed:—(1) The metals in the first and second cycles form no coloured solutions; in succeeding cycles the metals occupying the position of lowest atomic volume and the elements immediately succeeding them form coloured solutions. Thus, in the third cycle the metals from Ti to Cu, in the fourth cycle those from Nb to Pd, and in the fifth cycle the platinum group, Au and W, have this property. (2) The increments of atomic weight which, starting from hydrogen, successively give the



point where the atomic volume is a minimum, are members of a geometric series. T. C.

**Combination of Hydrogen and Oxygen by Electric Discharge.**

By P. P. DÉHÉRAIN and MAQUENNE (*Compt. rend.*, **93**, 965—966).—This is a continuation of previous work (*ibid.*, **93**, 895). As the degree of moisture has great influence on the nature of the electric discharge, the authors have studied the action of non-luminous discharges of weak currents both on aqueous vapour and on a moist mixture of hydrogen and oxygen, and have found that the same current decomposes water on the one hand, and causes the combination of hydrogen and oxygen on the other. A mixture of hydrogen and oxygen is obtained when an induction current (which under normal pressure gives a 5—25 mm. spark) in the form of the dark discharge is passed for a long time through rarefied tubes containing aqueous vapour, whilst when the same current is passed through tubes filled with a moist mixture of hydrogen and oxygen, a diminution in pressure is first observed, and after a time explosion occurs. T. C.

**Determination of Chemical Affinity.** By W. OSTWALD (*J. pr.*

*Chem.*, **24**, 486—497).—The author, finding that some of his results do not agree with Guldberg and Waage's theories on the influence of mass, has repeated the experiments with calcium chloride, oxalic, and hydrochloric acids. The method of procedure is: 5 c.c. hydrochloric acid (sp. gr. 0.4, containing 36.5 HCl in 0.4 litre) are poured by means of a fine pipette into a narrow-necked flask 25 c.c. cap. Variable quantities of either calcium chloride (or nitrate in nitric acid experiments) or oxalic acid are added, and the volume made up with water to 25 c.c. The liquid is poured into a test-tube containing a sufficient quantity of calcium oxalate, and immersed in a bath at 20° (in some experiments at 100°). After half an hour two portions of 10 c.c. are filtered off, and when a calcium salt has been used in the original liquid, the calcium oxalate in solution is directly determined with centinormal potassium permanganate. When oxalic acid has been used, the calcium oxalate is first precipitated with ammonia and then titrated. The author has repeated the experiments with more dilute solutions, and the results are arranged in eight tables, each containing from 16 to 20 determinations: they point to an error in the above-mentioned theory, which the author shows is not due to reaction. For with equal weights of calcium chloride or nitrate, or of oxalic acid employed, the same amount of calcium oxalate is dissolved, which shows that these salts react regularly. Dilution makes a slight but regular difference: hence the fault does not lie with  $\text{HCl} + \text{H}_2\text{O}$ ; and with calcium oxalate and water the combination is not sufficient to account for the digression. As his results have been conducted with great care, he thinks they must prove fatal to Guldberg and Waage's theory of the influence of mass. D. A. L.

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## Inorganic Chemistry.

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**Proportion of Carbonic Anhydride in the Upper Regions of the Atmosphere.** By A. MÜNTZ and E. AUBIN (*Compt. rend.*, **93**, 797—800).—The results of numerous carefully conducted determinations of the carbonic anhydride in air collected on the summit of the Pic du Midi in the Pyrenees (2877 metres) give 2·86 volumes in 10,000, or very nearly the same figure as the authors obtained in the plain of Vincennes. The carbonic anhydride therefore would seem to be uniformly diffused in the atmosphere, a confirmation of the views of Reiset and of Schläesing on this subject. R. R.

**Action of the Oxides of Nitrogen on Glass at a High Temperature.** By T. M. MORGAN (*Chem. News*, **44**, 253).—Several attempts were made to determine the nitrogen in organic nitro-derivatives by heating the substance in sealed tubes of hard glass containing oxygen, and in presence also of a little mercury to effect the reduction of any oxides of nitrogen that might be formed; but in all cases the nitrogen obtained was considerably less than the quantity theoretically present in the substance analysed. This is due to the action of the oxides of nitrogen on the glass, and also on the mercury if the temperature is below a dull red heat. A direct experiment on a new hard glass tube showed the formation of 3·8 mgrms. of soluble matter containing nitrates and nitrites. Other experiments gave 4·4, 2·2, and 4·8 mgrms. H. B.

**Action of Stannous Chloride on Nitrogen Compounds.** By O. v. DUMREICHER (*Monatsh. Chem.*, **1**, 724—754).—Stannous chloride in strongly acid solution does not act on nitrous oxide, but reduces nitric oxide to hydroxylamine, although not with sufficient readiness to form a serviceable method of preparing this compound. At a temperature of 100°, hydroxylamine is quickly and completely reduced to ammonia by excess of acid stannous chloride. Strong solutions of a nitrite and acid stannous chloride react violently, with formation of several gaseous products: in dilute solution the reaction proceeds quietly, nitrous oxide being evolved; this reaction is recommended for preparing pure nitrous oxide, the gas obtained containing no free nitrogen. Acid stannous chloride acting on nitric acid yields hydroxylamine, but the reaction proceeds further, and the hydroxylamine is nearly simultaneously reduced to ammonia. With ethyl nitrate, in alcoholic solution, the reaction proceeds very favourably, as much as 90 per cent. of the theoretical yield of hydroxylamine having been obtained.

*Estimation of Nitric Acid.*—Accurate results can be obtained by the following modification of Pugh's method. The substance is dissolved in the least possible quantity of water, and for each gram of nitric acid expected a solution of 16 grams of tin in 60 grams of 40 per cent. hydrochloric acid is added, and the mixture gently boiled for one

hour. The reduction is then complete, and the amount of ammonia formed can be estimated by the usual methods.

*Density of Nitrous Oxide.*—At 100°, the density of nitrous oxide agrees with that calculated from the molecular formula, but at lower temperatures there is a decided deviation. The mean results obtained were:—

	Density.
At 10° .....	1·52638
At 30° .....	1·52524
About 50° .....	1·52452
At 100° .....	1·52336    Calculated 1·52327

Very accurate results in estimating nitrous oxide can be obtained by explosion with hydrogen. A. J. G.

**Occurrence of Selenium and Tellurium in Japan.** By E. DIVERS (*Chem. News*, **44**, 229).—The sulphuric acid manufactured from sulphur from various parts of Japan, sometimes contains not inconsiderable quantities of selenium and tellurium. The flue deposits of the sulphur burners is also rich in selenium, and it is probable that considerable quantities of this element occur. H. B.

**Solidifying Points of Sulphuric Acid of Different Degrees of Concentration.** By G. LUNGE (*Ber.*, **14**, 2649—2650).—The author has made the following determinations of the solidifying and melting point of sulphuric acid of various degrees of concentration.

Specific gravity of acid at 15°.	Degrees Baumé.	Solidifying point.	Melting point.
1·671	58·00	Liquid at - 20°	—
1·727	60·75	- 7·5°	- 7·5°
1·732	61·00	- 8·5	- 8·5
1·749	61·80	- 0·2	+ 4·5
1·767	62·65	+ 1·6	+ 6·5
1·790	63·75	+ 4·5	+ 8·0
1·807	64·45	- 9·0	- 6·0
1·822	65·50	Liquid at - 20°	—

The solidifying point is the temperature at which crystals begin to separate out; this was constant in all cases, but the exact determination of the melting point was rendered difficult, owing to a continuous rise of the thermometer. V. H. V.

**Influence of the Temperature of the Voltaic Arc on Barium and Calcium Sulphates.** By ERÉMINE (*Bull. Soc. Chim.* [2], **36**, 556).—A mixture of equal parts barium and calcium sulphates is employed as the insulating material of the Jablochkoff candle. Under the influence of the high temperature of the arc, the barium sulphate volatilises, being probably first reduced and afterwards reoxidised. The calcium sulphate is reduced to the sulphide, which constitutes the greater part of the badly conducting "wick." At the same time gases are formed which act on oxidisable metals and colouring matters,

and when passed into a solution of potash yield potassium nitrite and nitrate, and ozone.  
C. H. B.

**Revision of the Atomic Weight of Cadmium.** By O. W. HUNTINGTON (*Chem. News*, **44**, 268—270).—The work was carried out after Cooke's method, and under his direction. That is, from a known weight of cadmium bromide, the silver bromide formed, and the metallic silver required were determined, thus affording a check of the accuracy of the work. The atomic weight at present accepted is a whole number. Pure cadmium bromide cannot be readily purified by recrystallisation, on account of its great solubility. The pure carbonate was prepared from the commercial metal by dissolving it in hydrochloric acid, precipitating as sulphide, redissolving as chloride, and then precipitating and digesting with a large excess of ammonium carbonate. The carbonate was twice precipitated in this way with ammonium carbonate, first from its solution in hydrochloric acid, and then in pure hydrobromic acid.

The hydrobromic acid was prepared from potassium bromide and sulphuric acid, and repeated distillation over potassium bromide. To test the purity of the materials, two sets of three experiments were made: (1) Conversion of a known weight of silver into bromide, gave mean 57·447 per cent. silver; and (2) reduction of a known weight of silver bromide to silver by a voltaic battery, gave mean 57·442 per cent. silver;  $\text{Ag} = 108$  and  $\text{Br} = 80$  requires 57·446. The cadmium carbonate was dissolved in the hydrobromic acid, and the product dried at  $200^\circ$ , and sublimed in a current of pure and perfectly dry carbonic anhydride. The lustrous crystals are not hygroscopic; some portions were twice sublimed. An amount of silver almost sufficient for the cadmium bromide taken was weighed, dissolved in nitric acid, and added gradually, the precipitation being finished by a standard solution of silver (1 gram per litre). The precipitate, after being washed with cold water, and collected by filtration with the reversed filter, was dried at  $120$ — $130^\circ$ , and weighed with the small filter. Eight experiments gave as mean  $\text{Cd} = 112\cdot31$  ( $112\cdot26$ — $112\cdot36$ ). In four of these cases the exact amount of silver required was also noted; these and four similar determinations gave as mean,  $\text{Cd} = 112\cdot32$  ( $112\cdot26$ — $112\cdot39$ ). A criterion of accuracy is obtained on comparing weights of silver bromide, 1·3808 gram formed from, and the silver, 0·7932 gram, required by a gram of cadmium bromide. These numbers are calculated from the means of the two series, and give  $\text{Ag}:\text{Br} = 108\cdot000:80\cdot006$ .  
H. B.

**Crystallisation of Cadmium and Zinc Sulphides.** By P. HAUTEFEUILLE (*Compt. rend.*, **93**, 824—827).—Crystals of cadmium sulphide are obtained by heating the amorphous substance in a porcelain crucible with alumina, on the surface of which the crystals are deposited. These crystals are frequently found to have different terminations at the two extremities of the principal axis, as is the case with greenockite, and the identity of the primitive forms can be proved by goniometric measurements. By this process, hexagonal blende is also obtained, and under certain conditions some of the

crystals are hemihedral like those of greenockite. The author has found that, under the influence of prolonged heating to bright redness, the elementary crystals composing zoned blende arrange themselves so that the crystals produced by their associations pass from rhombohedral to hexagonal symmetry.

R. R.

**Reactions of Gallium Salts.** By L. DE BOISBAUDRAN (*Compt. rend.*, **93**, 815—819).—This paper treats of the behaviour of certain salts of gallium, particularly with a view to a more advantageous method of separating it from zinc. The precipitation of gallium from a hydrochloric acid solution by potassium ferrocyanide is very complete, and the reaction is one of extreme delicacy. The author also recommends the substitution of iron for zinc in the precipitation of the solution obtained by treating blendes with *aqua regia*.

R. R.

**Preparation of Aluminium Iodide.** By G. GUSTAVSON (*Bull. Soc. Chim.* [2], **36**, 556).—A solution of aluminium iodide in carbon bisulphide or benzene may be readily obtained by mixing iodine and metallic aluminium in scraps, with three times their weight of the bisulphide or benzene in a tightly corked flask, kept cool by being placed in water, and allowing the mixture to stand three or four days with occasional agitation.

C. H. B.

**Action of Metallic Lead on Aqueous Solutions of Lead Nitrate.** By N. v. LORENZ (*Monatsh. Chem.*, **2**, 810—841). This reaction, first studied by Proust in 1821, afterwards by Berzelius (*Gilb. Ann.*, **40**, 186; **46**, 153), Chevreul (*Annales de Chimie*, **83**, 67; **84**, 5), Pelouze (*Lieb. Ann.*, **39**, 338), and Bromeis (*ibid.*, **72**, 38),\* has been further investigated by the author, who regards it as taking place by six stages, in which a molecule of normal lead nitrate,  $\text{Pb}(\text{NO}_3)_2$ , reacts successively with 1, 1 to  $1\frac{1}{4}$ ,  $1\frac{1}{4}$  to  $1\frac{1}{2}$ ,  $1\frac{1}{2}$  to  $1\frac{3}{4}$ ,  $1\frac{3}{4}$  to 2, and finally with more than 2 atoms of metallic lead.

*First Stage.*—When a solution of 50 g. lead nitrate,  $\text{Pb}(\text{NO}_3)_2$ , is boiled with 31.27 g. lead-turnings, the yellow liquid, after a quarter of an hour, deposits long colourless laminæ (I and II in the following table), the quantity of which goes on increasing for three-quarters of an hour. On continuing the action, yellowish-white needles having the same composition are also deposited, the laminæ almost disappearing after an hour and a half. On further prolongation of the action, the salt III separates in light yellow very thin oblique rhombic plates, the quantity of the preceding deposit diminishing at the same time. This third product attains its greatest development in  $2\frac{1}{2}$  hours, and is succeeded by lemon-yellow tablets (IV), which become abundant after six hours. In the *second stage*, there is formed a mixture of the salt V, with another of the same form, but of somewhat deeper yellow colour, the latter being exclusively formed when  $1\frac{1}{4}$  at. Pb is present to 1 mol. of the normal nitrate. In the *third stage*, laminæ are formed of continually darker colour, and approaching more and more nearly to the form of the elongated plates, while at the same time light

\* See also *Gmelin's Handbook*, Engl. Ed., **5**, 153—157.

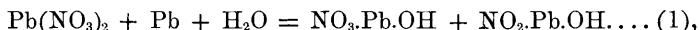
orange-coloured compact roundish needles appear, their quantity attaining its maximum when  $1\frac{1}{3}$ Pb is present to 1 mol.  $\text{Pb}(\text{NO}_3)_2$ , whilst that of the yellow tablets has diminished. The compounds formed in this reaction always appear in pairs, one component of which is represented by the formula VIb, VIc, VI $\bar{d}$ , or VI $\bar{e}$ , and the other by VII. In the *fourth* stage, if the solution be kept at the preceding strength (50 g.  $\text{Pb}(\text{NO}_3)_2$  in a litre of water), there is obtained, in addition to VI and VII, a basic nitrite IX, in compact rosettes of bright-red needles. In the *fifth* stage, if 2 at. lead are present to 1 mol. nitrate, the remaining lead becomes gradually covered with small crystals of the last-mentioned salt, and no further action takes place. The solution, as it cools, deposits a salt VIII, having the orange colour of VII, but in broader forms. In the *sixth* and last stage the product consists of a basic nitrite X, previously obtained by Pélilot and by Bromeis.

The composition of these several salts is shown in the following table, from which it will be seen that, as the action progresses, the relative amounts of base and nitrous acid continually increase. A stands for  $\text{NO}_3\cdot\text{Pb}\cdot\text{OH}$ ; B for  $\text{NO}_2\cdot\text{Pb}\cdot\text{OH}$ .

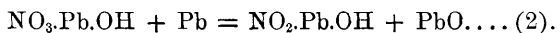
I and II.	$\text{NO}_3\cdot\text{Pb}\cdot\text{OH}$ .	VII.	$4\text{A} + 6\text{B} + 5\text{PbO}$
III.	$3(2\text{A} + \text{B}) + \text{H}_2\text{O}$ .		+ $\text{Pb}(\text{OH})_2$ .
IV.	$3(\text{A} + \text{B}) + 2\text{H}_2\text{O}$ .	VIII.	$2\text{A} + 4\text{B} + 3\text{PbO}$
V.	$6\text{A} + 7\text{B} + 4\text{H}_2\text{O}$ .		+ $\text{Pb}(\text{OH})_2$ .
VIa.	$3\text{A} + 5\text{B} + \text{H}_2\text{O}$ .	IX.	$\text{Pb}(\text{NO}_2)_2 + 2\text{PbO}$ , or
VIb.	$3\text{A} + 6\text{B} + \text{H}_2\text{O}$ .		$5\text{Pb}(\text{NO}_2)_2 + \text{NO}_2\cdot\text{Pb}\cdot\text{OH}$
VIc.	$3\text{A} + 9\text{B} + \text{H}_2\text{O}$ .		+ $10\text{PbO}$ .
VI $\bar{d}$ .	$\text{A} + 4\text{B}$ .	X.	$\text{NO}_2\cdot\text{Pb}\cdot\text{OH} + \text{PbO}$ .
VI $\bar{e}$ .	$\text{A} + 5\text{B}$ .		

The salts I, II, III have not been previously obtained by the reaction under consideration. VI $\bar{d}$  or VI $\bar{e}$  is very probably identical with the "heminitrite of lead" described by Bromeis. VII is certainly identical with the " $\frac{2}{7}$ -hyponitrate of lead" described by Bromeis, and VIII is probably identical with the salt to which he gives the formula  $\text{Pb}_7(\ddot{\text{N}} + \ddot{\text{N}}) + \ddot{\text{H}}_3$ , which is the same as  $\text{NO}_3\cdot\text{Pb}\cdot\text{OH} + 3(\text{NO}_2\cdot\text{Pb}\cdot\text{OH}) + 2\text{PbO} + \text{Pb}(\text{OH})_2$ ; but the quantity of nitrous acid contained in it is less than this formula requires. IX is probably Bromeis' "tribasic nitrite of lead," previously obtained by Berzelius; and lastly, X is the salt discovered by Pélilot, and described by Bromeis as "quadribasic nitrite of lead."

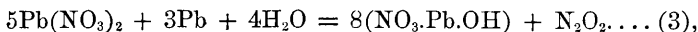
The formation of these several products is explained by the author as follows:—Berzelius observed that the action of lead on the normal nitrate at  $100^\circ$  is attended with evolution of nitrogen dioxide. Pélilot and Bromeis, on the other hand state, that between  $60^\circ$  and  $70^\circ$  no gas is evolved, the reaction taking place according to the equation:—



the basic nitrate, thus formed, reacting with the metallic lead, so as to form an additional quantity of basic nitrite and lead oxide, thus:—

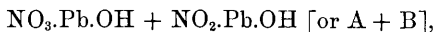


The quantities of lead oxide and basic nitrite continually increase, and these unite with the other constituents still present, forming polybasic compounds. According to the author's experiments, nitrogen dioxide is evolved both at 100° and 60°, and at the beginning of the action, basic nitrate is deposited free from nitrite, the reaction taking place according to the equation

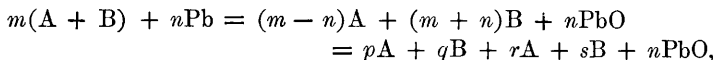


which therefore must hold good simultaneously with (1) from the beginning. Moreover, the formation of salt III cannot be explained without the use of equation (3).

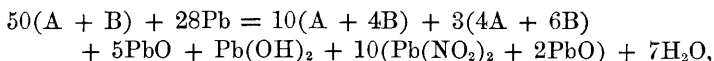
The simultaneous formation, during the stages 2, 3, 4, and 5, of monobasic double salts with gradually increasing proportion of nitrite, and of polybasic compounds, from  $m$  molecules of the group



and  $n$  molecules of lead, may be represented by the following general equation:—

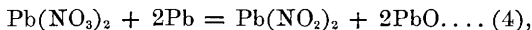


in which  $p, q, r, s$ , are arbitrary coefficients, but subject to the conditions that  $p + r = m - n$  and  $q + s = m + n$ , and that  $n$  must be smaller than or at most equal to  $m$ . In all special cases satisfactory equations may be obtained, thus:—

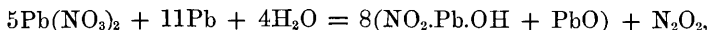


an equation which explains the complicated reaction in the fourth stage, resulting in the formation of the salts VI*d*, VII and IX (p. 365). A similar explanation may be given of the formation of VIII in the fifth stage. The salt VII may also be completely transformed into VIII.

The beginning of the sixth stage is characterised by the circumstance that 2 at. lead are dissolved in a liquid of concentration 1:50. This would lead to the equation



which, however, does not quite agree with the observed relations, inasmuch as a mixture of IX with the basic salt X is formed at this stage. This circumstance may however be explained by the simultaneous occurrence of the reaction (3) which, with equal quantities of lead, would give rise to the formation of a more highly basic nitrite than that resulting from (4). Since it has been proved that 5 mol.  $\text{Pb}(\text{NO}_3)_2$  can take up at most 11 atoms of lead, yielding as sole product the salt X, we obtain for the formation of salt X the equation



in connection with which the relations existing between the initial

and final conditions must be taken into account. This is easily done by supposing that the salt  $\text{NO}_3\cdot\text{Pb}\cdot\text{OH}$ , formed according to equations (1) and (3), is partly decomposed according to (2), producing the salt X, partly according to the equation  $2(\text{NO}_3\cdot\text{Pb}\cdot\text{OH}) + 3\text{Pb} = 5\text{PbO} + \text{N}_2\text{O}_2 + \text{H}_2\text{O}$ —which represents a continuation of reaction (3)—yielding lead oxide, which with the basic nitrite present, forms the salt X. A resolution of  $\text{NO}_2\cdot\text{Pb}\cdot\text{OH}$  into similar products, amongst which nitrogen monoxide would perhaps be found, is likewise consistent with the above-mentioned mode of formation of X. The final decision as to which of these two views is the true representation of the facts observed, must be deferred till a more exact investigation has been made of the gases evolved in these reactions. H. W.

**Iodides of Arsenic.** By D. BAMBERGER and J. PHILIPP (*Ber.*, 14, 2643—2648).—The authors find that Nicklès' method of preparing *arsenic tri-iodide* is the most convenient, viz., by heating arsenic and iodine in equivalent proportions in carbon bisulphide. Arsenic tri-iodide is soluble in most ordinary menstrua, but sparingly soluble in hydrochloric acid; it readily takes up oxygen, evolves iodine, and is converted into arsenious oxide (an analogous reaction occurs with sulphur). It is, however, far more stable in aqueous solution, from which it may be reprecipitated unchanged. On decomposing a hot hydrochloric acid solution of arsenious acid with a concentrated solution of potassium iodide, the tri-iodide separates out as a golden crystalline powder. If ammonia is passed into a solution of the tri-iodide in ether or benzene, a bulky white precipitate is thrown down, of composition  $2\text{AsI}_3\cdot 9\text{NH}_3$ . The tri-iodide, when heated with alcohol at  $150^\circ$ , yields ethyl iodide.

*Arsenic Di-iodide*,  $\text{AsI}_2$ .—The existence of phosphorus di-iodide and dihalogen compounds of bismuth, renders the existence of the corresponding arsenic compound probable: this the authors have succeeded in preparing by heating 1 part arsenic and 2 parts iodine, in sealed tubes to  $230^\circ$ ; a dark cherry-red crystalline mass is obtained, from which the di-iodide is separated by crystallisation from carbon bisulphide, in an atmosphere of carbonic anhydride. It is very readily oxidised, both in the solid state and in solution; on the addition of water it turns black, with separation of metallic arsenic, according to the equation  $3\text{AsI}_2 = 2\text{AsI}_3 + \text{As}$ ; this reaction distinguishes the di-iodide from the tri-iodide. It forms thin prismatic crystals of a cherry-red colour, but owing to their becoming opaque on exposure to the air, the measurement of their angles is rendered difficult; one of the angles, however, seems to correspond with one of the angles of the analogous phosphorus compound. V. H. V.

**Additional Experiments on the Atomic Weight of Antimony.** By J. P. COOKE (*Chem. News*, 44, 245—248).—The former determinations, fifteen in number, varied from 119.6—120.4, and the hope was expressed by the author that, after a thorough investigation of the subject, he might be able "to return to the problem with such definite knowledge of the relations involved as would enable us to obtain at once more sharp and decisive results than are now possible." The



antimony bromide was prepared as before, then repeatedly distilled, and the middle portion twice redistilled in a slow current of absolutely dry carbonic anhydride. A fresh preparation was used for every analysis, thus affording proof of its constant composition. The bromine was precipitated from the diluted tartaric acid solution by a slight excess of dilute silver nitrate solution, and the precipitate washed with lukewarm water by decantation and the use of the inverted filter. The precipitate, after being dried at  $120-130^{\circ}$ , and weighed, was always tested either by solution in strong aqueous ammonia or by fusing. Five experiments gave  $Sb = 120.08, 119.90, 119.93, 119.99, 120.08$ . A series of five volumetric determinations was made by adding to a dilute tartaric acid solution of the bromide exactly as much pure silver (after conversion into neutral nitrate and solution) as was required if  $Sb = 122$ , and then adding from a burette a solution containing 1 gram pure silver per litre; no indicator was used. The numbers obtained were  $Sb = 120.01, 120.02, 120.01, 119.98, 120.01$ . In the last two determinations the amount of precipitate formed was also weighed, and gave  $Sb = 120.01$  and  $120.00$ , also the check numbers  $Ag: Br = 108.00: 79.99$  and  $108.00: 80.01$ , mean  $80.00$ ; corresponding to the second decimal place with the determinations of Stas and Dumas.

The author has now given the following determinations of antimony bromide:—(1), fifteen, after crystallisation from carbon bisulphide, extremes  $119.4-120.4$ ; (2) five, after purification by distillation and sublimation, extremes  $119.90-120.08$ ; (3), five volumetrically, purified as No. 2, extremes  $119.98-120.02$ ; (4), two gravimetrically, connected with the last. The mean results are  $Sb = 120.00, 119.99, 120.01, 120.00$ ; final mean  $= 120.00$ , with  $Ag = 108.00$  and  $Br = 80.00$ . The previous thirteen determinations by the synthesis of the sulphide gave  $Sb = 119.94$ , when  $S = 32$ , and the seven analyses of the iodide gave  $Sb = 119.98$ , when  $I = 127.00$ . These results are important stages in the investigation, but add but little to the evidence of the far more accordant results since obtained. Lastly, the anomaly exhibited by the previous analyses of the chloride is explained by finding that the material contained a constant amount of oxychloride, and that the wash-water had a definite solvent action on the silver chloride.

H. B.

**Constitution of Complex Mineral Acids Derived from Tungstic Acid.** D. KLEIN (*Bull. Soc. Chim.* [2], **36**, 547—549).—The *boroduodecitungstates*,  $12WO_3.B_2O_3.4M_2O + nAq$ , and *tungstoborates*,  $9WO_3.B_2O_3.2M_2O + nAq$ , described by the author, are analogous in constitution to the *silicoduodecitungstates* and *tungstosilicates* of Marignac. By prolonged action of acids, especially hydrochloric, the boroduodecitungstates yield a deposit of tungstic hydrate, mixed with the more stable tungstoborates, not decomposed by acids. All borotungstates in presence of a slight excess of alkali give a paratungstate and polyborate.

In the hypothetical molecule of paratungstic acid,  $5H_2O.12WO_3 + nAq$ , there would appear to be eight OH groups which can be replaced only by bases, and two OH groups which may be replaced indifferently either by a basic radicle or by a monatomic radicle derived from a polybasic acid. This behaviour is similar to that observed in the

phenols. Thermochemical researches will probably show that the heats of combination with silica in the formation of silicotungstates and borotungstates are of the same order as the heats of etherification of the fatty acids. It would also be possible to determine whether the replacement of each of the first eight OH groups by a basic radicle develops more heat than the replacement of one of the last two OH groups by the same radicle.

C. H. B.

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## Mineralogical Chemistry.

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**Magnetism of the Nickeliferous Iron of Santa Catarina in Brazil.** By H. BECQUEREL (*Compt. rend.*, **93**, 794—797).—In a native iron found in 1875 in the province of Santa Catarina in Brazil, Lawrence Smith discovered a singular property, namely, that while in its natural state the mineral was but slightly attracted by the magnet, yet after having been heated to redness and allowed to cool, it manifested very powerful magnetic properties (*ibid.*, **92**, 848). The present paper gives the details of the author's examination of this phenomenon by help of his electromagnetic balance. The mineral contains 34 per cent. of nickel, and it was found that bars of pure nickel, electrolytically deposited in a crystalline condition, exhibited the same property in a degree which indicated the dissemination of that metal in the native iron as the cause of the latter's peculiar magnetic behaviour. We must conclude from this that the iron of the Brazilian mineral was crystallised at a low temperature; but this does not decide between the hypothesis of a meteoric and that of a terrestrial origin, for the mass might originally have been raised to a very high temperature, and then by a very slow molecular modification have crystallised at a low temperature, in the manner exhibited by certain irons.

R. R.

**Crystallography of a Variety of Blende.** By P. HAUTEFEUILLE (*Compt. rend.*, **93**, 774—777).—Besides the six characteristic cleavages of blende, the zoned crystals present three other planes of equally facile cleavage. It is only the three cleavages perpendicular to the plane of the layers that give large flat surfaces. In a blende formed of alternate red and yellow layers, the author found that the cleavage solid was the transposed rhomboidal dodecahedron having its axis parallel to the three cleavages which uninterruptedly intersect the two layers. The layers of crystals of blende are not therefore, like those of other minerals, evidence of mere intermittent accretion in a variable medium. Various complex optical properties of zoned blende are discussed in the paper.

R. R.

**Manganese Nodules and their Occurrence on the Sea Bottom.** By J. Y. BUCHANAN (*Chem. News*, **44**, 253—254).—Nodules from the South Pacific and from Loch Fyne were exhibited at the

British Association, also manganiferous worm tubes, and the mud in which they are both found; also cobalt nodules from New Carolina. By the dredge employed, not only is the soft surface layer taken, but also some underlying and stiffer material. A rich sample from Loch Fyne was found to contain 30 per cent. manganese nodules, 7.5 per cent. shells, and 62.5 per cent. sandy clay. The average weight of the nodules collected in 1878 was 1.7 gram. A sample collected, July, 1881, was passed through a sieve of  $\frac{1}{4}$  inch mesh; about 5 per cent. nodules (viz., 307) remained behind, having an average weight of 0.42 gram; the presence of but two pebbles amongst them is very strong evidence that they are formed *in situ*, and are not washed into their present position. Although the nodules are found only in certain localities, the manganese is frequently found coating shells and worm tubes. The nodules are comparatively soft, but harden on exposure to the air; when heated, they give off water, ammonia, and empyreumatic products; many have soft nuclei, richer in manganese oxide than the exterior portions. A considerable number of determinations have been made, both of the available oxygen and of the manganese, and if the manganese found be considered as united with the whole of the available oxygen, the resulting formula will vary between  $\text{MnO}_{1.5}$  and  $\text{MnO}_{1.6}$ . Taking the soft nucleus alone, and separated from the sandy coating, the formula is  $\text{MnO}_{1.75}$ ; the coating alone has the formula  $\text{MnO}_{1.5}$ . In some oceanic nodules the formula varied from  $\text{MnO}_{1.90}$  to  $\text{MnO}_{1.95}$ . Some of the Loch Fyne mud was found to contain 0.71 per cent.  $\text{MnO}$ , and a hardly distinguishable trace of extra oxygen.

The oceanic nodules contain 16—30 per cent. matter insoluble in acids; the Loch Fyne nodules, 28—33 per cent.; these insoluble residues contain 83—88 per cent. silica. The oceanic nodules contain more nickel and cobalt, but less copper than those of Loch Fyne. In the same dredgeful from Loch Fyne, nodules can be picked out which contain manganese oxides and only traces of ferric oxide, and others containing only ferric oxide. The author thinks that sufficient is known to indicate a probable process of production. The decomposition of animal matter in presence of the sulphates of the sea-water reduces these to sulphides, which in their turn react on the iron and manganese minerals (probably silicates) in the mud, forming sulphides of these metals. The author also thinks it probable that the shell-producing animals assimilate the lime from the sulphate as sulphide, in the interior of the animal, and transform this into carbonate on the outside.

H. B.

**New Sublimates from the Crater of Vesuvius.** By A. SCACCHI (*Gazzetta* 11, 488).—Of these sublimates the most abundant is a copper silicate of deep blue colour, which the author has named *neocyum*; it is always associated with white mamellated masses of silica: these two species are found sometimes adhering to the scoria, at others enveloped in the alkaline chlorides deposited on the same scoria. A third species, hitherto unobserved in the crater of Vesuvius, is formed of slender white crystals, covering the scoria, and similar in appearance to some kinds of felted amphibole. The underlying rocks are not decomposed,

and therefore seem to have had no part in the formation of these sublimate. There is, moreover, a fourth species of sublimate, consisting of very minute, yellowish-brown crystals. C. E. G.

**Presence of Titanium and Vanadium in all the Primitive Rocks.** By DIEULAFAIT (*Compt. rend.*, 93, 804—807).—A geological study of the bauxites, in which titanium and vanadium are known to exist in notable proportions, has led the author to the conclusion that bauxite originated from the disintegration of primitive granite rocks.

In rocks of this kind, therefore, titanium and vanadium should be found, and one result of the author's investigations is the demonstration of the existence of these substances diffused throughout all the primitive rocks. R. R.

**Deposits of Volcanic Tufa in the Province of Salerno.** By L. RICCIARDI (*Gazzetta*, 11, 480—485).—The author, after discussing the probable data to be assigned to the tufas of Salerno, gives analyses of three:—

I. The yellow coarsely granular deposit between Roccapiemonte and San Severino. It is compact and tolerably hard, but can be scratched with the nail. Sp. gr. 1·697 at 19°. Fuses before the blowpipe to a greenish glass.

II. The grey tufa of Fiano, which is very compact and hard enough to emit sparks with steel; augite, and a large quantity of leucite, is found interspersed in the mass. Sp. gr. 2·271 at 20°. Fuses before the blowpipe to a greenish-white glass.

III. A friable grey tufa from Pontefratta in the Irno valley, containing some leucite and a few fragments of augite. Sp. gr. 2·072 at 20°. Fuses before the blowpipe to a dark green glass.

	SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	Al <sub>2</sub> O <sub>3</sub> .	CaO.
I.....	63·14	4·10	0·76	17·34	5·91
II.....	62·62	0·75	4·30	17·34	3·23
III.....	61·81	1·44	3·80	19·86	3·75

	MgO.	Cl.	P <sub>2</sub> O <sub>5</sub> .	K <sub>2</sub> O.	Na <sub>2</sub> O.
I.....	2·57	traces.	0·09	3·89	1·58
II.....	1·05	„	0·19	8·34	2·03
III.....	1·55	„	0·24	5·73	1·79

C. E. G.

**Analysis of the Mineral Well at St. Anna, near Cernowic.** By F. FARSKY (*Bied. Centr.*, 1881, 785).—The water rises from the gneiss, and has a temperature of 5·5—8·8°, and a sp. gr. 1·000189 (at 17·5°C.).

In 100,000 parts there are—

Sodium chloride .....	0·6959 gram.
„ iodide .....	0·0138 „
Calcium sulphate .....	3·3077 grams
Potassium „ .....	0·2597 gram
Magnesium „ .....	0·2496 „
Acid calcium carbonate .....	1·5222 „
„ magnesium „ .....	0·7609 „
„ ferric „ .....	0·4503 „
Calcium phosphate .....	0·0104 „
Ferric oxide .....	0·1319 „
Silica .....	0·1003 „
Volatile matter (besides CO <sub>2</sub> ).....	0·2007 „
	<hr/>
	7·7034 grams.

E. W. P.

**The Blowing Wells near Northallerton.** By T. FAIRLEY (*Chem. News*, **44**, 242—243).—The air which comes from the wells is only atmospheric air without any excess of carbonic anhydride. During a rise of the barometer, an in-current of air, and during a fall, an out-current of air takes place. The sandstone in which the wells are sunk shows the air fissures; the currents are very powerful, producing a loud hissing noise in passing through the crevices. Noting the speed of the current with a vane anemometer, and the diameter of the large outlet-pipe, as also the heights of the barometer, the volume of the supposed air-cavities in the underlying magnesium limestone was found to be about 11,000,000 cubic feet. Using two very large dry gas-meters, the cavities were estimated at 10,000,000 cubic feet. Analyses of the water from this well—that at Solberge—and of the sandstone are given: the former is very hard from carbonates and sulphates of lime and magnesia, the latter also contains 7 per cent. carbonates of lime and magnesia.

H. B.

**Proportion of Potash to Soda in Natural Waters.** By C. CLOEZ (*Compt. rend.*, **93**, 41—44).—In the greater number of analyses of natural waters, the total amount only of alkalis (potash and soda) is given. With the view, however, of ascertaining the proportion between these two alkalis, the author has determined the quantity of each present in the waters used in Paris either for domestic purposes or for watering the roads. The potash was estimated as platino-chloride, and the soda as sulphate. The results recorded in the following table are calculated for 1 litre of water:—

	Total residue.	K <sub>2</sub> O.	Na <sub>2</sub> O.	$\frac{K_2O}{Na_2O} \times 100.$
Water taken from :—				
The Seine at the Port à l'Anglais ..	0·207	0·0014	0·0059	23·72
"    "    Pont Austerlitz ..	0·298	0·0012	0·0063	19·04
"    "    Pompe à feu de Chaillot .....	0·261	0·0015	0·0094	15·95
"    "    Machine de St. Ouen .....	0·259	0·0030	0·0109	27·61
The Marne at Saint Maur .....	0·319	0·0019	0·0070	27·14
"    the source of the Drain at the Machines of St. Maur.....	0·332	0·0025	0·0112	22·32
The Dhuis at its source .....	0·288	0·0005	0·0066	7·57
"    the reservoir of Menil- montant .....	0·260	0·0006	0·0078	7·68
The Vanne at the factory of Marlay de Roi .....	0·235	trace	0·0053	—
"    "    arrival tank of the reservoir of Mont- rouge.....	0·221	"	0·0064	—
Sources de Cochepie .....	0·256	0·0008	0·0048	16·66
Sources { from the Chaudron ....	2·821	0·0885	0·1196	73·99
du { "    Grandes-Rigoles ..	3·050	0·1320	0·1800	73·33
Nord. { "    Saint Martin ..	2·439	0·0167	0·1095	15·25
{ "    Morinwell ....	1·748	trace	0·0795	—
{ "    Moussins.....	1·936	"	0·0842	—

The proportion of potash to the total amount of alkalis present in the water is, with some exceptions, 1 to 5; and if it is admitted that the potash is derived from felspar rocks, the source of the soda must be looked for from another source; and since in the majority of cases the amount of chlorine found was exactly proportional to the amount of soda, it may be found in sodium chloride, which it must be admitted is contained in all the soils except those of granitic nature, whilst the strata of clay or marl contain the potassium salts.

This is borne out by the waters of the Seine and the Marne, the source of the former being the granitic rocks of Morvan, the latter plastic clay, and both contain potash. This is also the case with water of the Dhuis, the source of which is green marl, but the water of the canal leading to Paris, which is taken very near the source of the river, contains only very small quantities of potash. The waters of the sources of Cochevie also filter through clay, whereas those of the Vanne which flow through the chalk do not contain potash.

The sources of the Nord deviate from this rule, since although receiving its waters from the green marl, some contain large quantities of potash, and others only traces. It is to be remarked, however, that these waters contain large quantities of organic matter and nitrates, and before their entrance into Paris (as seen from the Morin well and the Moussins) do not contain any potash. It is, therefore,

probable that they receive their potash from the infiltration of water from Belleville.

L. T. O'S.

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## Organic Chemistry.

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**Boiling Points of Normal Saturated Hydrocarbons.** By M. I. GOLDSTEIN (*Jour. Russ. Chem. Soc.*, 1882, 45—46).—In a former paper (1879) the author has shown that the boiling points of saturated hydrocarbons are a function of three factors, viz., mol. weight, structure, and the relation between the number of carbon and hydrogen atoms in the molecule. The difference of the boiling points of two neighbouring saturated hydrocarbons,  $\text{CHMe}_2\text{R}$ , may be calculated from the formula  $19 + \frac{380}{n(n+1)}$ ,  $n$  being the number of carbon-atoms. If the boiling point of  $\text{CHMe}_2\text{CH}_2\text{CH}_3$  is  $30\cdot5^\circ$ , that of



will be  $62\cdot1^\circ$  (found  $62^\circ$ ), and that of  $\text{CHMe}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 = 90\cdot05^\circ$  (found  $90^\circ$ ). If the above suppositions are right, the differences between the boiling points of normal hydrocarbons and those constituted as above ought to be constant:—

			Difference.
Normal $\text{C}_5\text{H}_{12}$	$= 39\cdot0$	; isopropylethane . . .	$\text{C}_5\text{H}_{12} = 39\cdot5$ 8·5
„ $\text{C}_6\text{H}_{14}$	$= 70\cdot6$	; isopropylpropane ..	$\text{C}_6\text{H}_{14} = 62\cdot0$ 8·6
„ $\text{CH}_{16}$	$= 98\cdot65$	; isopropylbutane . . .	$\text{C}_7\text{H}_{16} = 90\cdot0$ 8·6

After the publication of the author's first paper, in which he calculated the boiling point of normal heptane to be  $= 98\cdot65^\circ$ , the b. p. of heptane from *Pinus sabiniana* was found by Thorpe to be  $98\cdot42^\circ$ .

B. B.

**Decomposition of Hydrocarbons of American and Caucasian Petroleums at Low Temperature.** By G. GUSTAVSON (*Ber.*, 14, 2619—2623).—The hydrocarbons of American and Caucasian petroleums do not behave towards aluminium bromide and hydrobromic acid like aromatic hydrocarbons; for on dissolving aluminium bromide in hydrocarbons obtained by fractionating American ligroin and Caucasian kerosin, and passing a stream of hydrobromic acid into the solution, the liquid separates into two layers. The constitution of the lower layer was in all cases found to be approximately the same, and the analyses point to the formula  $\text{AlBr}_3\text{C}_4\text{H}_8$ ; it is of the consistence of aqueous glycerol, of an orange-red colour, does not solidify at  $15^\circ$ , and at temperatures above  $120^\circ$  is decomposed with formation of gaseous hydrocarbons. An examination of the conditions of the reaction shows that the hydrobromic acid plays no part in the formation of the products, but only influences the rapidity of the reaction. The quantity of the lower layer is dependent on the quantities of hydro-

carbon and aluminium bromide used; with excess of the former, all the bromide is used up, and conversely with excess of the latter all the hydrocarbon enters into the reaction. Ethyl bromide may be substituted for hydrobromic acid without altering the product, the bromine of which at the end of the change exists as hydrobromic acid. Time and temperature are also most important factors in the reaction, which seems to proceed more rapidly the more complex the nature of the hydrocarbons. The hydrobromic acid seems to give with hexane ethyl bromide and butane, the former giving up hydrobromic acid in presence of aluminium bromide, so that, as a result of the reaction, unsaturated hydrocarbons and simpler homologues are obtained. This probably explains the presence of methane in petroleum, inasmuch as they must often come in contact with metallic chlorides and hydrochloric acid, and thus bears out the suggestion of Mendeleeff that the higher paraffins are decomposed into methane and olefines.

V. H. V.

**Transformation of Carbon Chlorides into Bromides.** By G. GUSTAVSON (*Bull. Soc. Chim.* [2], **36**, 556).—Carbon tetrachloride, tetrachlorethylene, and hexachlorethane are readily converted into the corresponding bromides by heating with aluminium bromide in a sealed tube at  $100^{\circ}$ . Carbon tetrachloride is almost entirely converted into the tetrabromide, but with the other chlorides the transformation is less complete. When any of the three chlorides is heated with metallic aluminium in presence of bromine, the only product is the hexbromide,  $C_2Br_6$ . In the case of  $CCl_4 + Br_2$ , the yield of  $C_2Br_6$  is feeble, and resinous products are formed, but no other bromo-derivative is produced.

C. H. B.

**Constitution of Nitroethane.** By I. KISSEL (*Jour. Russ. Chem. Soc.*, 1882, 40—44).—The author studied the action of acid chlorides on the sodium derivative of nitroethane. V. Meyer (*Ann.*, **171**, 48, and *Berl. Ber.*, **6**, 1169) failed to obtain a satisfactory result in this way.

If small quantities of sodium-nitroethane are added to a solution of benzoic chloride in benzene, a violent reaction takes place. On treating the pasty product of the reaction with boiling benzene, sodium chloride is left behind, and on evaporating the solution in a desiccator, it yields two substances: (1) A solid body which, after treatment with petroleum and recrystallisation from alcohol, gives white crystals of Lossen's dibenzhydroxamic acid,  $(C_6H_5CO)_2NHO$ ; (2) a light brown oil which consists chiefly of diacethydroxamic acid,  $(CH_3CO)_2NHO$ . Acetic chloride and sodium-nitroethane give a solid body, which is the hydrochloride of hydroxylamine, and a liquid product: diacethydroxamic acid. The author proceeds to investigate the reaction between acid chlorides and sodium derivatives of secondary nitro-compounds of the fatty series.

B. B.

**$\beta$ -Chlor-allyl Chloride and some of its Derivatives.** By P. v. ROMBURGH (*Bull. Soc. Chim.* [2], **36**, 549—557).—Acrolein may be readily obtained by strongly heating 100 grams potassium hydrogen

sulphate and 50 grams glycerol in a flask holding 1500 c.c., and collecting the distillate in a flask surrounded by ice. The aqueous layer is separated from the supernatant acrolein by means of a separating funnel. Similar quantities of potassium hydrogen sulphate and glycerol are introduced into the still warm flask, and heated in the same way. By this method only the first quantity froths up, and 300 grams glycerol may be treated in the same flask. The aqueous portions of the several distillates are mixed and distilled in order to recover dissolved acrolein. The acrolein is agitated with lead oxide, and dried over calcium chloride. The yield of pure optically inactive acrolein amounts to 33—35 per cent. of the weight of glycerol taken.

Treated with phosphorus pentachloride, acrolein yields chlorinated products which the author divided into two fractions, one boiling below  $120^{\circ}$ , the other above. The fraction boiling below  $120^{\circ}$  may be separated into two portions: the first, *allylidene chloride*, b. p.  $85^{\circ}$ ; vapour-density, 3.825 (air = 1). It is optically inactive, and when treated with chlorine in excess yields *allylidene tetrachloride*, b. p.  $179-180^{\circ}$  at 756.6 mm.; sp. gr. at  $15^{\circ}$  = 1.521; vapour-density 6.05. When heated with a saturated aqueous solution of hydrochloric acid in sealed tubes at  $100^{\circ}$  for 10 hours, allylidene chloride is converted by intermolecular change into  $\beta$ -chlor-allyl chloride.

The second portion is  $\beta$ -chlor-allyl chloride,  $C_3H_4Cl_2$ , a colourless optically inactive liquid; b. p.  $109-110^{\circ}$  (corr.); sp. gr. at  $15^{\circ}$  = 1.226; vapour-density 3.825. When treated with chlorine in excess, it yields a tetrachloride, b. p.  $179-180^{\circ}$  at 756.6 mm.; sp. gr. at  $15^{\circ}$  = 1.522; vapour-density 6.21, identical with the allylidene tetrachloride obtained from allylidene chloride.

When symmetrical dichlorhydrin is treated with phosphoric anhydride, it yields a liquid which boils at  $180^{\circ}$  under a pressure of 766.4 mm., and not at  $171^{\circ}$  as stated by Hartenstein. It is identical with the allylidene tetrachloride obtained from allylidene chloride and  $\beta$ -chlor-allyl chloride. The constitution of the latter is therefore  $CH_2Cl.CH:CHCl$ , as stated by Friedel and Silva, and not  $CH_2Cl.C\ddot{C}.CH_2Cl$  as assumed by Hartenstein.

$\beta$ -Chlor-allyl alcohol,  $CHCl:CH.CH_2OH$ , is obtained by heating  $\beta$ -chlor-allyl chloride with aqueous potash, drying the distillate over potassium carbonate, and purifying by fractionation. It is a colourless liquid, with a pungent odour and burning taste, and blisters the skin. B. p.  $153^{\circ}$  (corr.); sp. gr. at  $15^{\circ}$  = 1.162; vapour-density 3.3. It is very slightly soluble in water, combines directly with bromine, and reacts violently with nitric acid and phosphorus pentachloride.

The method of Carius is not applicable to the determination of the halogen in the above chlorides, since they are only attacked with great difficulty by nitric acid.

C. H. B.

**General Method of Preparing Secondary Alcohols.** By G. WAGNER (*Bull. Soc. Chim.* [2], 36, 306).—The author prepares secondary alcohols by the general method of acting on the aldehydes with organo-zinc compounds. He has given particular attention to the action of zinc ethyl on valeral and benzaldehyde. The reaction takes place at the ordinary temperature. Beyond the production

of ethylisobutylcarbinol (b. p. 146—148°) in one case, and of ethylphenylcarbinol (b. p. 218°) in the other, there was no formation of other secondary products. According to Rieth and Beilstein, the above aldehydes only give condensation-products with formation of water. Although the aldehydes studied belong to different homologous series, and differ greatly in their properties, they all yield secondary alcohols, which proves that the method is of general application.

J. I. W.

**Action of Zinc Ethide and Methide on Chlorinated Aldehydes.** By G. WAGNER (*Ber.*, **14**, 2556—2557).—Methylallylcarbinol is probably formed by the action of zinc on a mixture of acetaldehyde and allyliodide. The author complains that Garzarolli-Thurnlach has encroached on his (the author's) subject in his work on the action of zinc ethide on chlorinated aldehydes, in a recent number of the *Annalen*.

W. C. W.

**Action of Carbonic Oxide on Monosodium Glyceride.** By W. F. LOEBISCH and A. LOOSS (*Monatsh. Chem.*, **2**, 782—795).—Sodium glyceride, prepared by the action of sodium ethylate on anhydrous glycerol, has the composition  $C_3H_7NaO_3, C_2H_5O$ , but may be freed from crystal-alcohol by prolonged heating in a stream of hydrogen; when this dealcoholised glyceride is heated at 180° in a stream of carbonic oxide, a distillate is obtained consisting chiefly of propylene glycol,  $C_3H_8O_2 = OH.CHMe.CH_2.OH$  (b. p. 189°; sp. gr. 1·047 at 19°), together with small quantities of carbonic, formic, and normal butyric acids, and methyl alcohol, these products being nearly the same as those which Belohoubek obtained by the dry distillation of glycerol with sodium hydroxide (*Abstr.*, 1880, 232).

H. W.

**Preparation of Disodium Glyceride.** By W. F. LOEBISCH and A. LOOSS (*Monatsh. Chem.*, **2**, 842—844).—To prepare this compound, a weighed quantity of monosodium glyceride containing alcohol of crystallisation was pulverised as finely as possible under absolute alcohol, and added to the calculated quantity of sodium ethylate dissolved in alcohol. (To 1 gram sodium there correspond 2·95 grams  $C_2H_5ONa$  and 6·95 grams alcoholated monosodic glyceride,  $C_3H_7O_3Na + C_2H_5O$ .) The mixture was boiled in a reflux apparatus for several hours in a stream of hydrogen, and finally heated at 180° to expel the alcohol. The disodium glyceride then remained in dry, dazzling white finely porous lumps, which easily crumbled to a crystalline powder, attracting moisture from the air with great rapidity, and deliquescing to a caustic syrup. For preservation, the lumps must be kept in a vessel filled with hydrogen, and having its mouth turned downwards. An analysis of the recently prepared compound gave 34·3 per cent. sodium; another made some days later gave 32·8; the formula  $C_3H_5Na_2O_3$  requires 33·82 per cent.

Disodium glyceride melts at 220°, giving off bubbles at the same time; on heating it to 270°, a brown liquid distils over.

H. W.

**Glycerol Diformin.** By P. v. ROMBURGH (*Compt. rend.*, **93**, 847—849).—In the preparation of diformic acid by distilling dehydrated oxalic acid with glycerol, a residue is obtained, which, on being shaken with ether and the ether evaporated, leaves a yellowish liquid; this, after being freed from formic acid and rectified under diminished pressure (20 mm.), was found to consist in great part of glycerol diformin. The diformin is a colourless neutral liquid (b. p. 163—166°; sp. gr. 1.304 at 15°), soluble in ether, alcohol, and chloroform, but insoluble in carbon bisulphide. Water decomposes it into glycerol and formic acid. It is decomposed by distillation at the ordinary pressure, yielding water, carbonic anhydride, and allyl formate.

In most text-books, the conversion of oxalic acid into formic acid when it is heated with glycerol, is explained by supposing the formation of monoformin as an intermediate product. The author, on the contrary, thinks that it is the diformin which yields the formic acid; as he found that diformin is not converted into triformin when it is heated with dehydrated oxalic acid, but carbonic anhydride is given off, and the yield of formic acid obtained corresponds with the quantity of oxalic acid employed.

When diformin is heated with glycerol (5 parts) at 220°, carbonic oxide and anhydride are evolved, and allyl alcohol distils over, accompanied by traces of formic acid and allyl formate. C. E. G.

**Decomposition of Grape-sugar and Uric Acid by Alkalis.** By M. NENCKI and N. SIEBER (*J. pr. Chem.*, **24**, 498—506).—On digesting grape-sugar with potash at 35—40° for some time, it is decomposed into lactic acid and an acid of unknown constitution, insoluble in ether, but soluble in alcohol. Lactic acid is produced at this temperature, also with soda, tetramethylammonium hydroxide, neurine, &c., but not with ammonia, sodic carbonate, guanidine, creatine, &c. Milk-sugar and maltose undergo a similar change with alkalis, whilst cane-sugar, mannite, &c., are not altered. Uric acid is quickly decomposed under similar conditions, going through the stages of decomposition from uroxanic acid to carbonic anhydride and ammonium oxalate. The authors remark that perhaps neurine is in some way connected with the formation of lactic acid in living organisms.

D. A. L.

**Temperature at which Invertin is Destroyed.** By A. MAYER (*Bied. Centr.*, 784).—Invertin is prepared from yeast, by first exhausting with alcohol, then carefully pounding it up with water and fine sand, after which it is exhausted with water; from the aqueous extract alcohol precipitates the invertin, which may be dried over sulphuric acid. Dried invertin can be heated to 100° without harm, but its solution is rendered inactive at 51—55°, according to the degree of concentration. If the solution consists of 50 per cent. of glycerol, then a temperature of 50—60° is necessary to destroy its action; whereas the presence of alcohol lowers the temperature by 10°.

E. W. P.

**Hydrocellulose and its Derivatives.** By A. GIRARD (*Ann. Chim. Phys.* [5], **24**, 337—384).—Celluloid substances often undergo, under various circumstances, a remarkable modification in their

physical state. Their flexibility and natural elasticity disappear, and they become brittle and easily reducible to powder. By the action of mineral and even vegetable acids, cellulose,  $C_{12}H_{10}O_{10}$ , before becoming saccharified, is transformed by hydration into a new compound,  $C_{12}H_{11}O_{11}$ , which the author terms hydrocellulose. It closely resembles cellulose, but differs from it by its extreme brittleness.

*Preparation of Hydrocellulose.*—The methods of preparing hydrocellulose may be divided into three general classes:—1. The immersion of the celluloid material in a powerful and concentrated acid. 2. The exposure of the material to acid vapours. 3. Methods dependent on the employment of weak acid solutions requiring a more or less prolonged contact, or a temperature above the normal one. The author has treated the following substances by each of the methods, and finds that the ultimate product is the same for all, cotton, flax, hemp, jute, paper, wood, elder pith.

*Preparation by Immersion in Concentrated Acids.*—The mineral acids alone have the power of transforming cellulose into hydrocellulose by simple immersion. The reaction proceeds most easily with sulphuric acid. It is less energetic with phosphoric acid. Organic acids do not form hydrocellulose at all in this manner. If sulphuric acid is employed, its strength should be carefully determined. It is most convenient to use acid of sp. gr. 1.453. The fibre is immersed in it at  $15^{\circ}$ , and allowed to remain 12 hours. Hydrochloric acid, when used at  $21^{\circ}$  B., transforms the fibre into hydrocellulose in 24 hours. Hydriodic, hydrobromic, and hydrofluoric acids behave in a similar manner in aqueous solutions. When nitric acid at  $43^{\circ}$  B. is employed, the product consists of a mixture of hydrocellulose and nitrocellulose: weaker acid fails to yield any considerable quantity of hydrocellulose. When cellulose is immersed in syrupy phosphoric acid, it is only very slightly modified.

*Preparation of Hydrocellulose by the Action of Hydrated Gaseous Acids.*—Cold moist hydrochloric acid gas transforms cellulose into hydrocellulose in about an hour. When employed warm and moist, the reaction is complete in a few minutes. The author states that the action of hydrochloric acid on cellulose has afforded him the means of establishing with certainty the nature of the phenomena resulting in the production of hydrocellulose. Hydrobromic and hydriodic acids exactly resemble hydrochloric acid in their behaviour towards cellulose. In the formation of hydrocellulose by hydriodic acid, a certain quantity of iodine is deposited on the fibre. On washing with water, a splendid blue colour resembling that of iodide of starch is produced. An excess of water removes the colour, but a fresh quantity of iodine solution restores it. Hydrofluoric acid yields hydrocellulose readily in the cold. Under the same circumstances, nitric and sulphuric acids at the ordinary temperature only very tardily produce a modification. Carbonic and sulphurous anhydrides and hydrogen sulphide, when pure, have no effect.

*Preparation of Hydrocellulose by Dilute or Weak Acids.*—Dilute solutions of sulphuric, hydrochloric, nitric, and phosphoric acids (1 in 100, for example), when employed to saturate cellulose, effect the transformation into hydrocellulose in from two to three months, if

after immersion the fibre is left in the air at the ordinary temperature. The action is complete in one month when a 3 or 4 per cent. solution is employed. If, however, the solution is heated to 60—70°, a few hours is sufficient. A one per cent. solution of the acid, at the above temperature, renders the cellulose completely friable in a few hours.

*Action of Organic Acids.*—The author immersed pieces of cotton in 5 per cent. solutions of oxalic, tartaric, and citric acids, then dried them in the air, and afterwards heated them in closed vessels at 100°. The sample treated with oxalic acid was completely changed; that with tartaric acid only partially, and the one with citric acid still less. Acetic and formic acids exercise a moderate action on cellulose.

*Action of Salts which easily lose part of their Acid.*—The author shows that the theory of the modification of celluloid substances by direct dehydration and carbonisation by the dehydrating power of certain salts ought not to be admitted, since it is to the direct action of acids liberated from the salts when in contact with vegetable matter that the phenomenon is due. He shows that it is only at relatively high temperatures and by a secondary action that carbonisation takes place.

*Action of Strong Alkalis on Celluloid Matter.*—On treatment with a strong solution of potash, the fibre of cotton becomes swollen or "mercerised." It then possesses the property of becoming blue with iodine, like that treated with sulphuric acid. No hydrocellulose, however, is formed. The swollen fibre presents the same appearance under the microscope as that acted on by sulphuric acid.

Hydrocellulose, however it may be prepared, always has the same composition. It is a fine white powder, which oxidises rapidly on application of heat or prolonged exposure to the air. Samples for analysis were always dried by the author in a vacuum, or in a current of some inert gas. He states that hydrocellulose is to be regarded as a carbohydrate intermediate between cellulose and glucose. Its production from the former is due to direct hydration, the necessity for the presence of water affording a decisive proof thereof. The author states that in no case could he obtain the theoretical yield of hydrocellulose, and he found on examination that its production is always accompanied by that of glucose. Hydrocellulose is characterised by its great friability. It differs from cellulose in the greater sensibility which it exhibits towards all reagents. It can best be distinguished from cellulose by the facility with which it is oxidised. When heated in sealed tubes at 180° with sulphuric acid (5 per cent.), cellulose dissolves completely in 8 or 10 hours, yielding a solution which is almost colourless, and evolving no gas. Hydrocellulose also dissolves, but leaves an abundant deposit of carbon, and on opening the tube, there is a copious disengagement of gaseous products. Heated in sealed tubes with seven or eight times its weight of acetic anhydride, hydrocellulose dissolves instantly, as soon as the temperature reaches 180°; whilst two or three hours are required to dissolve cellulose. It is remarkable that dye-stuffs which can only with great difficulty be made to colour ordinary cellulose, possess a great affinity for hydrocellulose.

*Conversion of Hydrocellulose into Friable Pyroxylin Compounds.*—Cellulose and hydrocellulose yield identical nitro-compounds. The author concludes that the hydrocellulose is dehydrated before it is nitrated. It yields only the same amount of nitro-compounds as cellulose. He finds that the yield of pyroxylin is greater when the hydrocellulose is not employed in the form of powder.

He also points out that the rotting of window curtains in towns is probably due to the production of hydrocellulose by the action of the hydrogen sulphide and sulphurous anhydride in the air. He also attributes the dry rotting of wood to the production of the same substance by the action of acids generated by the fermentation of saccharine matter.

J. I. W.

**Suggestions respecting the Nomenclature of Carbonic Acid Derivatives.** By A. BERNTHSEN (*Annalen*, **211**, 85—99).—The author, after noticing that the nomenclature of these compounds is somewhat confused, the same body being in many instances called by several different names—the acid  $\text{HS.CO.OH}$ , for example, being designated as *Monothiocarbonic*, *Thiocarbonic*, *Oxysulphocarbonic*, *Carbonyloxy-sulphonic*, and *Sulphodioxycarbonic acid*—proposes a systematic nomenclature based upon the following rules:—

1. Acids containing the group *Carbonyl*: $\text{C}:\text{O}$  to be called, as at present, *Carbonyl acids*.

2. Acids containing *Thiocarbonyl*: $\text{C}:\text{S}$  to be called *Thiocarbonyl acids*.

3. Acids isomeric with the carbonic and thiocarbonic acids, and containing the group  $\text{:C:NH}$ , to be called *Imidocarbonic acids*.

4. The group  $\text{NH}_2.\text{CO}$ — to be denoted by the prefix *Carbamin-*, and  $\text{NH}_2.\text{CS}$ — by *Thiocarbamin-*; and accordingly  $\text{NH}_2.\text{C}(\text{NH})$ — by *Imidocarbamin*.

5. The prefix “mono” to be in most cases expressed.

These rules lead to the following names for the primary substances, the derivatives of which are either known compounds, or certain classes of bodies not yet known, but theoretically possible. Names which agree with those already in use are marked with a \*; those which differ from existing names with a †.

(1.)	$\text{HO.CO.OH}$ * Carbonic acid.	$\text{HS.CO.OH}$ † Carbonyl-monothioic acid.	$\text{HS.CO.SH}$ * Carbonyl-dithioic acid.
(2.)	$\text{HO.CS.OH}$ * (Mono)-thiocarbonic acid.	$\text{HS.CS.OH}$ * Dithiocarbonic (thiocarbomonothioic) acid.	$\text{HS.CS.SH}$ * Trithiocarbonic (thiocarbodithioic) acid.
(3.)	$\text{NH}_2.\text{CO.OH}$ * Carbamic acid.	$\text{NH}_2.\text{CO.SH}$ *† Carbamin(mono)thioic acid.	
(4.)	$\text{NH}_2.\text{CS.OH}$ * (Mono)thiocarbamic acid.	$\text{NH}_2.\text{CS.SH}$ * Dithiocarbamic (thiocarbaminthioic) acid.	



- |      |  |  |   |
|------|--|--|---|
| (5.) | HO.C(NH).OH<br>Imidocarbonic acid.               | HS.O(NH).OH<br>Imidocarbomonothioic acid.              | HS.C(NH).SH<br>Imidocarbodithioic acid. |
| (6.) | NH <sub>2</sub> .C(NH).OH<br>Imidocarbamic acid. | NH <sub>2</sub> .C(NH).SH<br>Imidocarbaminthioic acid. |   |
| (7.) | NH <sub>2</sub> .CO.Cl<br>† Carbamine chloride.  | NH <sub>2</sub> .CS.Cl<br>Thiocarbamine chloride.      |   |

No derivatives of imidocarbonic or imidocarbamic acid are at present known, but their discovery may be confidently anticipated.

The bracketted names assigned to three of the above compounds are more systematic than their synonyms, and lead more readily to appropriate names for the more complex derivatives; the others have, however, the advantage of agreeing with those already in use. The names proposed for the compounds in the seventh line do away with the inappropriate term "urea chloride."

This nomenclature is in accordance with that of the isomeric *thiamides*, called by the author *imido-thioethers*, *e.g.*,—benzimidothioethylether, C<sub>6</sub>H<sub>5</sub>.C(NH).SC<sub>2</sub>H<sub>5</sub>,—which are derived from the imido-thio-acids, R.C(NH).SH, and these again from the imido-acids R.C(NH).OH, ethers of which are also known.

*Supplementary Rules for the Nomenclature of Compounds derived from those in the preceding Table.*—(1.) The names of ethers, acid and neutral, may be formed from those of the acids, according to established usage, *e.g.*, EtS.CS.OEt, *diethyl dithiocarbonate*; EtS.CO.SMe, *ethyl methyl carbonyldithioate*; EtS.CO.SH, *ethyl-carbonyldithioic acid*, &c. To distinguish between pairs of isomeric alcoholic acids, as (a) EtS.CO.OH and (b) HS.CO.OEt, or (c) EtS.CS.OH and HS.CS.OEt, or finally their ethers, the name of the radicle attached to S may be placed immediately before the prefixes "thio, monothio, dithio," the bracketted names in the preceding table being employed: thus the compound (a) will be called *carbonyl-ethylthioic acid*; (b) *ethyl-carbonylthioic acid*; (c) *thiocarbonylthioic acid*; (d) *ethylthiocarbothioic acid*; MeS.CS.OEt, *ethylc thiocarbomethylthioate*.

(2.) *Carbamic acids* (Nos. 3 and 4 in table) and the corresponding chlorides (No. 7) may be named according to previous usage, the names of the radicles which replace the amidic hydrogen being placed at the beginning of the word: *e.g.*, MePhN.CS.OH = *Methylphenylthiocarbamic acid*; Me<sub>2</sub>N.CO.Cl, *Dimethylcarbamic chloride*. The names *urethane, thiomethane*, &c., may be retained as convenient collective terms.

(3.) In the names of *Imidocarbonic acids* (No. 5), the radicle which replaces the hydrogen of the NH-group is also to be placed first.

(4.) In naming *Imido-carbamic acids*, the name of the radicle which enters into the imidogen-residue is to be placed before the prefix "imido" at the beginning of the word; that of the radicle which enters the amido-group, before the prefix "carbamin"; *e.g.*, PhHN.C(NEt).SH = *Ethylimido-phenyl carbaminthioic acid*; similarly H<sub>2</sub>N.C(NH).SC<sub>2</sub>H<sub>5</sub> = *Benzylc Imidocarbaminthioate*, or more shortly *Imidocarbaminthiobenzyl*.

Compounds are also known which are derived from the several carbonic or carbamic acids by elimination of  $H_2O$  or  $H_2S$ : *anhydrides* or *disulphide-compounds*, e.g.,  $CO_2H.S.COOH$ , *dicarbothioic acid*;  $NH_2.CS.S.CS.NH_2$ , the so-called "thiuram sulphide," which may be conveniently called *thiocarbamine sulphide*; the name "thiuram" proposed by Hlasiwetz and Kachler for the group  $CS.NH_2$  not having been generally adopted. The so-called "thiuram disulphide,"  $NH_2.CS.S_2.CS.NH_2$ , may be called *carbamine disulphide*, and the compound,  $EtO.CS.S_2.CSOEt$  (ethyl dioxysulphocarbonate, ethyl disulphocarbonate sulphide), may be named *xanthic disulphide*.

H. W.

**Etherification of Polybasic Acids.** By N. MENSCHUTKIN (*Ber.*, 14, 2630—2632).—A continuation of the author's researches on the etherification of isobutyl alcohol by acids (*Abstr.*, 1881, 884). The following results were obtained with the dibasic acids of formula  $C_nH_{2n}(COOH)_2$ :—

	Initial velocity.	Limit.
Succinic acid, $COOH.(CH_2)_2.COOH$ .....	42·94	70·18
Normal pyrotartaric acid, $COOH.(CH_2)_3.COOH$ ..	50·21	73·91
Pyrotartaric acid, $COOH.CHMe.CH_2.COOH$ ....	42·85	73·51

Although the conditions of formation of an ethereal salt of a polybasic acid are more complex than in the case of monobasic acids, yet the phenomena observed are perfectly analogous. The initial velocity and the limit of etherification of polybasic acids is higher than those of saturated monobasic acids containing the same number of carbon-atoms. The etherification of the pyrotartaric acids shows that isomerism has no influence on the limit, but only on the initial velocity, which is higher in primary acids than in primary secondary acids. Terephthalic acid, as monobasic tertiary acid, has too small an initial velocity for determination; and even after 384 hours, only 25 per cent. of the acid is etherified. Of unsaturated dibasic acids, fumaric and maleic acids gave values differing from one another, like those of the two pyrotartaric acids.

	Initial velocity.	Limit.
Fumaric acid.....	32·69	73·56
Maleic acid .....	51·45	72·69

These values show that maleic acid is a primary acid as represented  $CH_2.COOH$

by Fittig's formula,  $\begin{array}{c} | \\ <C.COOH \end{array}$ .

Citraconic acid and its isomerides also differ in their initial velocity values.

	Initial velocity.
Citraconic acid .....	47·42
Mesaconic acid .....	35·88
Itaconic acid .....	27·97

It is probable that citraconic acid contains a carboxyl group in the primary position.

Camphoric acid possesses the property of a tertiary acid, its initial velocity being 9·56, its limit at the end of 21 days being 69·47; the formula proposed by Ballo for this acid (Abstr., 1881, 415) is most in accordance with these determinations.

The values found for hydrophthalic acid were, initial velocity, 21·86, limit, 73·44, which show that it is not a tertiary, but probably a secondary acid, and that the two hydrogen-atoms introduced into phthalic acid combine with those carbon-atoms to which the carboxyl groups are attached.

V. H. V.

**Influence of the Molecular Weight of Homologous Bodies on the Course of Incomplete Reactions.** By N. MENSCHUTKIN (*Jour. Russ. Chem. Soc.*, 1882, 19—36).—In previous papers (abstracted in this Journal) the author gave an account of his researches on the etherification of organic acids and alcohols, especially as regards the *limit* of the two inverse reactions (*a*) formation of an etheric salt from the acid and alcohol; (*b*) decomposition of the resulting salt by the water formed in the reaction (*a*); and the rate of formation of etheric salts.

In the present paper the author endeavoured to ascertain whether those reactions follow the law of homologous bodies. In the former papers, the experimental results were given in percentages, or molecular limits (percentage of alcohol and acid converted into the etheric salt, or the number of molecules formed from 100 parts of the alcohol and 100 parts of the acid). The results can be also given in *molecular-weight limits*, which relate to the quantities of alcohols and acids, represented by their molecular weights. If the percentage limit of the ethyl-acetic system is = 66·57, the molecular-weight limit of ethyl-alcohol is =  $\frac{66\cdot57 \times 46}{100} = 30\cdot62$ , that of acetic acid is  $\frac{66\cdot57 \times 60}{100} = 39\cdot94$ . Thus the molecular-weight limits of acids in the *isobutylic system* are:—

		Homologous difference.
Acetic acid. . . . .	40·42	} 10·41
Propionic acid . . . . .	50·83	
Normal butyric acid. . . . .	61·17	
		} 9·90 = $\frac{19\cdot81}{2}$
„ caproic acid. . . . .	80·98	
„ octylic acid . . . . .	102·05	} 10·53 = $\frac{21\cdot07}{2}$

The difference of these limits in the isobutylic series is constant at 10·29, and the limits may be calculated by means of the formula:  $a + (n - 2)d$ , where  $a$  = molecular-weight limit of acetic acid = 40·42,  $n$  = number of the members of the series,  $d$  = 10·29. Thus the molecular-weight limits of acids in the isobutylic system are:—

	Calculated.	Found.
Acetic acid .....	40·42	40·42
Propionic acid .....	50·71	50·83
Normal butyric acid.....	61·00	61·17
„ valeric acid .....	71·29	not known
„ caproic acid .....	81·58	80·98
„ heptylic acid .....	91·87	not known
„ octylic acid .....	102·16	102·05

The same agreement is seen in a table giving the percentage limits:—

	Calculated.	Found.
Acetic acid.....	67·38	67·38
Propionic acid .....	68·52	68·70
Normal butyric acid.....	69·32	69·52
„ valeric acid .....	69·89	—
„ caproic acid.....	70·33	69·81
„ heptylic acid .....	70·67	—
„ octylic acid.....	70·65	70·87

The molecular-weight limits of acids in the ethylic systems are given by the formula  $33·94 + (n - 2) 10·29$ .

	Calculated.	Found.
Acetic acid .....	39·94	39·94
Propionic acid .....	50·23	—
Normal butyric acid.....	60·52	60·51
„ valeric acid .....	70·81	—
„ caproic acid.....	81·10	80·96
„ heptylic acid .....	91·39	—
„ octylic acid .....	101·68	—

The percentage limits in the ethylic series are:—

	Calculated.	Found.
Acetic acid.....	66·57	66·57
Propionic acid .....	67·88	—
Normal butyric acid.....	68·77	68·77
„ valeric acid .....	69·42	—
„ caproic acid.....	69·91	69·80
„ heptylic acid .....	70·30	—
„ octylic acid .....	70·61	70·09

The differences between the percentage limits of etherification of homologous acids with one and the same alcohol decrease with increasing molecular weight of the acids:—

	Ethylic systems.	Isobutylic systems.
Acetic acid. . . . .	—	—
Propionic acid. . . . .	1·31	1·14
Normal butyric acid . . . . .	0·89	0·80
„ valeric acid . . . . .	0·65	0·57
„ caproic acid . . . . .	0·49	0·44
„ heptylic acid. . . . .	0·39	0·34
„ octylic acid . . . . .	0·31	0·28

In the case of higher members of the homologous series of acids, the percentage limits of etherification will therefore most probably be equal.

The molecular-weight limits of alcohols in the acetic systems are given by the formula  $30·62 + (n - 2) 9·62$ .

	Mol. weight limits.		Per cent. limits.	
	Calculated.	Found.	Calculated.	Found.
Ethyl-acetic system . . . .	30·62	30·62	66·57	66·57
Propyl-acetic „ . . . .	40·24	40·11	67·06	66·85
Butyl-acetic „ . . . .	49·86	49·86	67·38	67·38
Amyl-acetic „ . . . .	59·48	—	67·59	—
Hexyl-acetic „ . . . .	69·10	—	67·74	—
Heptyl-acetic „ . . . .	78·72	—	67·86	—
Octyl-acetic „ . . . .	88·34	—	67·95	—

The differences between the percentage limits decrease with increasing molecular weight of the alcohols, thus:—

0·49      0·32      0·21      0·15      0·12      0·09

so that the limits will probably be equal in the case of higher members of the series.

The homologous differences of molecular-weight limits of acids in different systems are  $= 10·29$ , but those of alcohols increase slightly with increase in molecular weight of the acid, and approach the value  $10·29$  of acids, thus:—

In acetic ethers . . . . .	9·62
„ propionic ethers . . . . .	9·74
„ normal butyric ethers . . . . .	9·82
„ „ valeric ethers . . . . .	9·89
„ „ caproic ethers . . . . .	9·94
„ „ heptylic ethers . . . . .	9·98
„ „ octylic ethers . . . . .	10·01

In the following paragraph the author shows how the limits of etherification of any system of alcohols and acids may be calculated by using the above-mentioned formula,  $a + (n - 2)d$ .

Starting from the molecular-weight limits of acids, the value  $d$  remains constant, being  $= 10·29$ , the values of  $a$  are:—

	Value of $\alpha$ .
Ethyl-acetic system.....	39.94
Propyl-acetic „ .....	40.23
Butyl-acetic „ .....	40.42
Amyl-acetic „ .....	40.55
Hexyl-acetic „ .....	40.64
Heptyl-acetic „ .....	40.71
Capryl-acetic „ .....	40.77

Starting from the molecular weights of alcohols, the case becomes more complicated, the values of  $a$  and  $d$  being both different.

	Value of $\alpha$ .
Aceto-ethyl ether.....	30.62
Propiono-ethyl ether .....	31.22
Normal butyl-ethyl ether .....	31.63
„ valero-ethyl „ .....	31.93
„ capro-ethyl „ .....	32.15
„ heptyl-ethyl „ .....	32.33
„ capryl-ethyl „ .....	32.48

	Value of $d$ .
Acetic ethers .....	9.62
Propionic ethers .....	9.74
Normal butyric ethers.....	9.82
„ valeric „ .....	9.89
„ caproic „ .....	9.94
„ heptylic „ .....	9.98
„ octylic „ .....	10.01

The above rules only refer to combination of eight acids with eight alcohols, but the first members (formic acid and methylic alcohol) show exceptional values.

The author's results, as regards the rate of etherification of normal acids and alcohols (the quantities of compound ether formed after the first hour of the reaction), are of a similar character. The molecular-weight rates of etherification of alcohols in the acetic systems may be calculated from the formula  $21.52 + (n - 2) 6.53$ .

	Calculated.	Found.
Ethyl alcohol.....	21.52	21.52
Propyl „ .....	28.05	27.90
Butyl „ .....	34.58	34.66
Octyl „ .....	60.70	60.54

Even the absolute rates obey the law of homologous bodies, as is seen from the following four hour-rates, which show equal homologous differences = 8.43, thus:—

	Mol. weight velocities.	Homologous difference.
Ethyl alcohol .....	29.31	8.36
Propyl „ .....	37.67	
Octyl „ .....	80.31	$8.53 = \frac{42.64}{5}$

The law of the influence of the molecular weights of acids upon the rate of formation of (isobutylic) ethers cannot yet be found, as is seen from the following numbers:—

	Mol. weight velocities in isobutyl systems.
Acetic acid .....	26·61
Propionic acid .....	30·47
Normal butyric acid .....	29·26
„ caproic „ .....	38·37
„ octylic acid .....	44·43

From the above examples it follows that not only the chemical and physical properties of bodies, but also their complete and partial reactions, obey the laws of homologues. B. B.

**Decomposition of some Metallic Acetates in presence of Water.** By J. RIBAN (*Compt. rend.*, **93**, 1140—1143).—Since formic acid has been shown by Berthelot to be an endothermic body, and acetic acid on the contrary to be formed with disengagement of heat, it follows that the latter should not be so readily attacked by bodies which easily decompose the former. This is borne out by the results obtained by the author in treating metallic acetates under similar conditions to the formic salts (*ibid.*, 1023 and 1082) when the acetate is merely resolved into a metallic oxide and the free acid. In all cases, except otherwise stated, 10 c.c. of a 5 per cent. solution of the acetate was heated at 175° in a closed vessel free from air.

Manganese, cobalt, nickel, iron and zinc acetates begin to decompose after four or five hours' heating, but even after 70 hours' heating the decomposition into oxide and acid is only partial, MnO being formed in small, and Co(HO)<sub>2</sub> and Ni(HO)<sub>2</sub> in large quantities. ZnO is formed in the case of zinc. Ferrous acetate yields black FeO owing to the decomposition of the water, and 2 to 5 c.c. of hydrogen per gram of anhydrous substance used, according to the time of heating, a small quantity of the ferrous oxide being converted into the magnetic oxide. After 100 hours' heating, a 2 per cent. solution of uranium acetate yields acetic acid, and the oxide U<sub>2</sub>O<sub>3</sub>·2H<sub>2</sub>O crystallising in six-sided prisms or plates, which do not allow the passage of the polarised ray when the principal planes of the prisms are parallel or perpendicular to the principal axis of them, or when the light travels along the same axis. The same substance grouped in spherulites viewed with polarised light presents the black cross observed in the case of chalcidony and other members of the hexagonal system.

Neutral lead acetate undergoes no decomposition, but the tribasic acetate is decomposed with formation of monoxide.

The formation in the first place of cupric oxide and acetic acid, and the subsequent combustion of acetic acid, with formation of carbonic anhydride and cuprous oxide, when copper acetate is heated with water, as shown by Cazeneuve (*Abstr.*, 1881, 153) is also borne out by the author's results, the cuprous oxide being crystalline.

Mercuric and silver acetates, after prolonged heating, give acetic

acid, carbonic anhydride, and metallic mercury and silver. The silver acetate is particularly stable, some remaining undecomposed even after 50 hours' heating. L. T. O'S.

**Influence of Heat and the Proportion of Glycerol on the Decomposition of Oxalic Acid.** By LORIN (*Compt. rend.*, 93, 1143—1145).—In continuation of his researches on the decomposition of oxalic acid the author has increased the proportion of acid to glycerol from 1—4 to 3—1.

On heating at 100°, 1 mol. of glycerol, and adding 1 mol. oxalic acid from time to time, the acid first loses water of crystallisation, then formic acid and water of etherification are formed, and carbonic anhydride evolved. The formic acid unites with the glycerol, and by adding further quantities of oxalic acid, part of the formic acid in combination is liberated, and a further quantity of formic acid is produced, part of which unites with the glycerol, while part remains in the free state. This reaction continues until a point is reached at which the quantity of formic acid produced is equivalent to the oxalic acid used. After six additions of oxalic acid a mixture of mono- and di-formin is obtained. During the process about 1 per cent. of carbonic oxide is evolved.

The quantitative results given in detail show that large quantities of oxalic acid may be converted into formic acid by a small quantity of glycerol.

By starting with formin and anhydrous oxalic acid, formic acid of 98 per cent. may be obtained.

The etherification of the formic and oxalic acids is produced by a secondary reaction. L. T. O'S.

**Conversion of Fumaric into Maleic Acid.** By A. PICTET (*Ber.*, 14, 2648—2649).—The author alludes to the ready conversion of maleic acid into its isomeric fumaric acid, and the difficulty experienced in effecting the reverse change. For this, the following indirect method is proposed: fumaric acid heated with excess of water at 150—200° is converted into malic acid (Jungfleisch, *Ber.*, 12, 370), which by distillation is decomposed into fumaric acid and maleic anhydride, and the latter by distillation with water is converted into malic acid, whilst the fumaric acid remaining in the retort is again converted into malic acid, and the process of distillation, &c., repeated. The malic acid from the fumaric acid is optically inactive, is not deliquescent, and melts at 105—108°; it is probably identical with the acids obtained by Pasteur from inactive aspartic acid, and by Kekulé from monobromosuccinic acid, but isomeric with that obtained by Loidl (*Ber.*, 11, 1244) by heating fumaric acid with soda. The author endeavoured, but without success, to separate this acid by means of its cinchonine salts into dextro- and lævo-malic acids. The author considers it probable that there are two modifications of inactive malic acid corresponding to racemic and inactive tartaric acid.

V. H. V.

**Argento-antimonious Tartarate (Silver Emetic).** By J. P. COOKE (*Chem. News*, 44, 233—234).—Wallquist and Dumas and Piria



have obtained this salt only in the amorphous state. The author was the first to obtain it crystalline, as described in a previous paper, viz., on adding an excess of silver nitrate to a concentrated solution of antimonious chloride and tartaric acid. He now finds that 1000 parts of water at 15° dissolve 2.68 to 2.76 parts, and at 100°, 10 parts of the salt. Hence the fear that the silver chloride, bromide, or iodide precipitates formed under these circumstances, unless the solution be very concentrated, might contain an admixture of silver emetic is unfounded. By solution in hot water and cooling, beautiful crystals can be obtained with an almost adamantine lustre. The formula  $C_4H_4O_6AgSbO + H_2O$  requires 26.34 per cent. silver; a mean of three analyses gave 26.30 per cent. At 200° it decomposes with slight explosion, spangles of silver and a powder of antimonious oxide remaining of nearly the theoretical weight. The crystals are rhombic and hemihedral. Forms observed  $\frac{P}{2} \cdot \infty P \infty \cdot \infty P$ . and perhaps  $P \infty$ . The axial relations are  $a : b : c = 1 : 1.386 : 0.571$ .

H. B.

**Researches on Petroleum from Caucasus.** By MARKOWNIKOFF and OGLOBLIN (*Jour. Russ. Chem. Soc.*, 1882, 36—40).—In a previous paper, the authors have shown that the high-boiling portions of Caucasus petroleum, after the separation of oxygen compounds, have the composition  $C_nH_{2n-2}$ , and that on boiling with iodine, after the separation of hydrocarbons rich in carbon, hydrocarbons  $C_nH_{2n}$  remain behind. In order to study the hydrocarbons, which have been destroyed by iodine, fuming sulphuric acid was used, by which process sulphonic acids of the hydrocarbons were obtained. Thus the portion of naphtha boiling at 180—200° contains beside a small quantity of the hydrocarbon  $C_{11}H_{16}$ , the hydrocarbons  $C_nH_{2n}$ , and as the chief admixture, isomerides of cymene, metamethylpropylbenzene, and probably also durenene. The portion boiling at 240—250° contains one of the modifications of propylnaphthalene, then  $C_{12}H_{14}$  and  $C_{11}H_{14}$ , the last belonging probably to the styrene series, and finally  $C_{15}H_{30}$ . The authors have reason to suppose that the aromatic hydrocarbons exist as such in the petroleum, and are not formed by the action of the sulphuric acid. Although the petroleum, when it is boiled, gives off gaseous products, the authors do not agree with Mendelejeff, that a decomposition takes place, but consider the gases as being in solution in the liquid: for butylene, as the authors found, is easily dissolved by the heavy rock oil, and given off completely only on heating to 250°.

B. B.

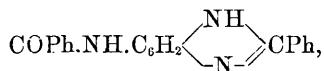
**Methylation of Benzene by Methyl and Aluminium Chlorides.** By O. JACOBSEN (*Ber.*, 14, 2624—2636).—The author has examined the products obtained by the successive introduction of the methyl group into toluene, by Friedel and Crafts' method of synthesis, and has obtained results differing from those of Ador and Rilliet (Abstracts, 1879, 228, 527). This methylation is effected under the same conditions with equal facility in the case of isomeric hydrocarbons, but more easily the greater number of methyl groups already introduced. The product of the methylation of toluene was separated into

two fractions, one boiling at 133—143°, the other at 155—170°. From the former by the action of sulphuric acid, and subsequent neutralisation with barium carbonate, barium paraxylenesulphonate was obtained, which was converted into terephthalic acid. The greater part of the barium salts consists, however, of the orthoxylenesulphonate, which was recognised by its amide, and by its conversion into orthophthalic acid. Although the author was unable to isolate derivatives of metaxylene, yet its presence must be inferred, inasmuch as the mesitylene obtained from the higher fraction could not be formed by the methylation of ortho- or para-xylene. This synthesis offers a ready method for the preparation of orthoxylene from toluene. Metaxylene yields a pseudocumene and mesitylene by methylation, and ortho- and para-xylene yield pseudocumene only. Further, mesitylene yields isodurene, together with penta- and hex-methylbenzene; pseudocumene yields durene; both durene and isodurene are easily converted into penta- and hex-methylbenzene. The products formed from toluene are collected in the following table:—

Toluene	Orthoxylene	Pseudocumene . Durene—	Penta- and hex- methylbenzene. V. H. V.
	Paraxylene		
	Metaxylene		
		Mesitylene . . . . Isodurene	

**Derivatives of Metadiamidobenzene and Orthoparadiamidotoluene.** By S. RUHMANN (*Ber.*, **14**, 2651—2659).—In the course of investigations carried out with the view of isolating a triamidobenzene, the author has prepared the following derivatives of metadiamidobenzene

*Dibenzoylmetadiamidobenzene*,  $C_6H_4(NH\bar{B}z)_2$ , formed by the action of benzoic chloride on metadiamidobenzene hydrochloride, crystallises in white needles (m. p. 240°) sparingly soluble in alcohol, soluble in acetic acid. Its *nitro*-derivative,  $C_6H_3NO_2(NH.COPh)_2$ , crystallises in needles (m. p. 222°), sparingly soluble in alcohol; this, on reduction with tin and hydrochloric acid, gives an anhydro-base—



crystallising from alcohol in white leaflets, which soften at 125°, and melt completely at 214°. The formation of this anhydro-base shows that the nitro-group and one of the benzoyl groups are in contiguous positions, and the nitro-derivative has the composition

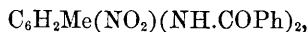
$$[NH\bar{B}z : NH\bar{B}z : NO_2] = [1 : 3 : 4],$$

or  $[NH\bar{B}z : NO_2 : NH\bar{B}z] = [1 : 2 : 3]$ . The nitrodibenzoyl compound, on treatment with alcoholic potash, yields a nitrodiamidobenzene, identical with that obtained by Barbaglia; but it was not found possible to convert this into a triamidobenzene.

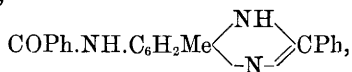
*β-Dinaphthylmetadiamidobenzene*,  $C_{10}H_7(NH.C_{10}H_7)_2$ , prepared by the action of β-naphthol on metadiamidobenzene, crystallises in violet interlaced needles (m. p. 126°), soluble in alcohol, benzene, ether, &c. By heating metadiamidobenzene hydrochloride with fuming

sulphuric acid at  $170^{\circ}$ , a sulphonic acid is formed, identical with that obtained by Post and Hardtung (Abstracts, 1880, 395). By decomposing the potassium salt of this acid by Griess' reaction, *chrysoïlinesulphonic acid*,  $\text{PhN} : \text{N} \cdot \text{C}_6\text{H}_2(\text{NH}_2)_2 \cdot \text{HSO}_3$  is formed, which crystallises in compact needles, sparingly soluble in water and alcohol. Its barium salt forms golden-red needles, and its sodium salt, golden glistening needles. This compound is isomeric with the sulphonic acid obtained by Will directly from chrysoidine.

*Derivatives of Orthoparadiamidotoluene.*—By heating diamidotoluene with benzoic chloride, *dibenzoyldiamidotoluene*,  $\text{C}_6\text{H}_3\text{Me}(\text{NHBz})_2$ , is formed, which crystallises in tables (m. p.  $224^{\circ}$ ), sparingly soluble in alcohol, soluble in acetic acid. Its nitro-derivative,



crystallises in citron-yellow needles (m. p.  $245^{\circ}$ ); it yields on reduction an anhydrous base,



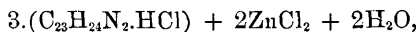
which crystallises in white needles (m. p.  $218^{\circ}$ ). On heating nitro-dibenzoyldiamidotoluene with alcoholic potash, a *nitrodiamidotoluene* (m. p.  $254^{\circ}$ ) is obtained, which on reduction with tin and hydrochloric acid, is converted into *triamidotoluene hydrochloride*,



which separates out as a white crystalline precipitate. On decomposing this salt with sulphuric acid, a deep blue solution is obtained, from which *tridiamidotoluene sulphate* separates out. Triamidotoluene is a triacidic base, and thus differs from triamidobenzene, which is diacidic. Considering the formation of the anhydro-base of the nitro-dibenzoyl derivative, triamidotoluene must possess the constitution  $[\text{Me} : \text{NH}_2 : \text{NH}_2 : \text{NH}_2] = [1 : 2 : 3 : 4]$ , or  $[1 : 2 : 4 : 5]$ .

*Monobromodiamidotoluene*, obtained by the bromination of dibenzoyldiamidotoluene and subsequent removal of benzoyl groupings with alcoholic potash, crystallises in faintly coloured needles (m. p.  $104^{\circ}$ ), soluble in alcohol and ether. V. H. V.

**Condensation Products of Tertiary Aromatic Bases.** By O. FISCHER (*Ber.*, 14, 2520—2529).—In addition to those salts of benzaldehyde-green, previously described by the author (*Annalen*, 206, 129), the oxalate  $2 \cdot \text{C}_{23}\text{H}_{24}\text{N}_2 + 3\text{C}_2\text{H}_2\text{O}_4$ , and zincchloride,



were prepared, and were found to be identical with the compounds obtained by Doebner (*Ber.*, 13, 2224) from malachite-green.

*Tetrazyldiamidotriphenylcarbinol*, prepared from diethylaniline and benzaldehyde, yields an oxalate crystallising in golden prisms. This salt loses its golden lustre when dried over sulphuric acid; the dried salt has the composition  $\text{C}_{27}\text{H}_{32}\text{N}_2 + \text{H}_2\text{C}_2\text{O}_4 + \text{H}_2\text{O}$ . The compound  $\text{C}_6\text{H}_4(\text{OH}) \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , is prepared by heating at  $100^{\circ}$  a mixture

of salicylaldehyde (10 parts), dimethylaniline (22—25 parts), and zinc chloride (20 parts). When the mixture no longer smells of salicylaldehyde, the excess of dimethylaniline is distilled off in a current of steam, and the residue recrystallised from hot alcohol. The substance forms needle-shaped crystals (m. p. 127°), soluble in boiling alcohol and benzene. It unites with hydrochloric and sulphuric acids to form crystalline salts. It dissolves in dilute soda-lye, but on the addition of concentrated soda-lye to this solution, a bulky precipitate is thrown down. The acetic derivative  $C_{23}H_{25}N_2O\dot{A}c$ , crystallises in iridescent plates (m. p. 144°). The sulphate or hydrochloride yields *salicylaldehyde-green* on oxidation with manganese or lead peroxide.

If paroxybenzaldehyde is substituted for salicylaldehyde in the preceding reaction, a condensation product is obtained, having the composition  $C_{23}H_{26}N_2O$ . This substance melts at 163°, forming a red liquid. It is soluble in alcohol, benzene, toluene, and in dilute soda-lye. The acetic derivative  $C_{23}H_{25}N_2O\dot{A}c$ , is deposited from an alcoholic solution in colourless prisms (m. p. 146°). On oxidising the condensation-product with manganese dioxide, it yields a green solution, which appears reddish-violet by transmitted light. Paper stained with this solution is turned violet by dilute acids. Dilute alkalis restore the original green colour.

*Paranitrobenzaldehyde*, first prepared by O. Fischer and P. Grieff (*Ber.*, 13, 670), is deposited from hot water in colourless prisms (m. p. 106°) soluble in alcohol, benzene, and glacial acetic acid. It sublimes without decomposition, and can also be distilled in a current of steam. It is easily decomposed by reducing agents, but is not readily attacked by oxidising agents. On the addition of ammonia to the aldehyde, a crystalline precipitate is thrown down, which changes into a red amorphous powder.

With aniline, paranitrobenzaldehyde unites to form the crystalline compound,  $NO_2.C_6H_4CHNPh$  (m. p. 93°), soluble in benzene and light petroleum.

*Paranitrotetramethyldiamidotriphenylmethane*,  $C_{23}H_{25}N_3O_2$ , is prepared by the action of zinc chloride on a mixture of dimethylaniline and paranitrobenzaldehyde. The crude product is repeatedly boiled with water, dilute hydrochloric acid, and finally with dilute alcohol. On dissolving the residue in hot toluene, and diluting the solution with half its volume of alcohol, the pure compound is obtained in golden plates (m. p. 176°). It unites with acids, forming colourless salts, and combines directly with methyl iodide to form the crystalline compound  $C_{23}H_{25}N_3O_2.2MeI + H_2O$ , which melts with decomposition at 220°.

*Tetramethylparaleucaniline*,  $C_{23}H_{27}N_3$ , is prepared by the action of zinc-dust on a solution of the nitro-base in hydrochloric acid. It is precipitated from the solution by excess of ammonia, and is purified by dissolving the washed precipitate in benzene. Light petroleum is added to this solution to precipitate resinous impurities; the filtrate deposits the leuco-base in glistening plates. On oxidation with lead or manganese dioxide, tetramethylpararosaniline, a violet-red colouring matter, is obtained.

*Paranitrotetramethyldiamidotriphenylcarbinol*,  $C_{23}H_{25}N_2O_3$ , obtained by

the action of manganese dioxide and dilute sulphuric acid on paranitrotetramethyldiamidotriphenylmethane, is identical with the *paranitrobenzaldehyde-green*, previously described by E. and O. Fischer (*Ber.*, **12**, 800).  
W. C. W.

**Conversion of Azoxybenzene into Oxyazobenzene.** By O. WALLACH and L. KIEPENHEUER (*Ber.*, **14**, 2617—2619).—It has already been shown by one of the authors that azoxybenzene ( $\text{C}_6\text{H}_5\text{N})_2\text{O}$ , when heated with sulphuric acid to a moderate temperature, is converted into a substance, probably identical with oxyazobenzene,  $\text{PhN}:\text{N}.\text{C}_6\text{H}_4.\text{OH}$  (*Abstr.*, 1880, 556). In the present communication, the authors establish the identity of these substances by a comparison of their acetyl-derivatives, the nitro-phenols obtained from them, and the product of the action of phosphorus pentachloride on them. This latter reaction gives rise to a substance crystallising in orange-yellow needles,  $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_2$  (m. p.  $145^\circ$ ), insoluble in water, sparingly soluble in alcohol.

It has been suggested by Kekulé that this substance is an oxyazobenzene,  $\text{PhN}-\text{N}.\text{C}_6\text{H}_4.\text{OH}$ , but in that it is insoluble in alkalis, and



does not yield an acetyl-derivative, it is probable that it does not contain a hydroxyl grouping combined with a carbon-atom. An examination of the reaction between phosphorus pentachloride and oxyazobenzene showed that an intermediate phosphorus compound was first formed, which on treatment with water or alkalis yielded the substance  $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_2$ . The author proposes to investigate this point by further experiments.  
V. H. V.

**Action of Phosphorus Pentachloride on Diphenylacetamide and Diphenylbenzamide.** By O. WALLACH (*Ber.*, **14**, 2611—2616).—In the course of some controversial remarks, the author quotes experiments made in association with Kamensky on the action of phosphorus pentachloride on substituted amides, in which the hydrogen-atoms directly combined with the nitrogen, have been replaced by various groups. By the action of phosphorus pentachloride on diphenylacetamide, a base of composition  $\text{C}_{26}\text{H}_{22}\text{N}_2$  is obtained, which gives an amorphous grey platinochloride; with diphenylbenzamide, resinous substances were produced from which no new base could be extracted.  
V. H. V.

**Compounds of Phenyl Thiocarbimide with Acid Amides.** By E. BAMBERGER (*Ber.*, **14**, 2651).—This paper is a preliminary notice with regard to a series of compounds obtained when the amides are heated for some time with phenyl thiocarbimide: a combination takes place and triclinic crystals separate out. It appears that these compounds are not thiocarbimides in which the hydrogen is replaced by an acid radicle, inasmuch as they dissolve easily in alkalis and in alcohol, and are reprecipitated from the latter on adding water. Ammoniacal solutions of silver do not remove sulphur from them, even

when heated. The author is examining the reaction of the amides of various acids, carbamide, thiocarbamide, and cyanamide.

V. H. V.

**Action of Guanidine Carbonate on Phenylthiocarbimide in presence of Water.** By E. BAMBERGER (*Ber.*, **14**, 2638—2643).—By the action of phenylthiocarbimide on guanidine carbonate in the presence of aqueous alcohol, diphenylthiocarbamide is formed, besides guanyphenylthiocarbamide, the proportion of the former increasing according to the degree of dilution of the alcohol. The phenylthiocarbimide then undergoes a reaction analogous to that of the corresponding carbimide,  $2\text{SCNPh} + 2\text{H}_2\text{O} = \text{SC}(\text{NHPh})_2 + \text{CO}_2 + \text{H}_2\text{S}$ . The author investigates the part played by this guanidine carbonate in the decomposition of the phenylthiocarbimide. From experiments on the decomposition of guanyphenylthiocarbamide by phenylcarbimide and water, he concludes that guanyphenylthiocarbamide is first formed by the action of phenylthiocarbimide on guanidine, and that it splits up into carbonic anhydride, hydrogen sulphide, aniline, and guanidine, the latter combining with a fresh quantity of the thiocarbimide to reproduce the guanythiocarbamide, while the aniline combines also with the thiocarbimide to form diphenylthiocarbamide. Thus the guanythiocarbamide is successively regenerated and destroyed, and theoretically a given quantity of guanidine carbonate could convert an indefinite quantity of the phenylthiocarbimide into the thiocarbamide; in practice, however, this result is never obtained, owing to secondary decompositions. The guanidine carbonate in the addition of water to the thiocarbimide according to the reaction above, plays a part analogous to that of sulphuric acid in the continuous ether process.

V. H. V.

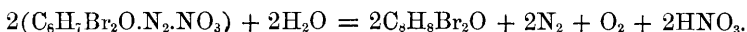
**Direct Production of Phenol from Benzene.** By C. T. KINGZETT (*Chem. News*, **44**, 229—230).—In a recent paper A. R. Leeds described the production of phenol from benzene by digestion with dilute hydrogen peroxide. Benzene is not capable of directly absorbing oxygen like the terpenes. The author wished then to ascertain if phenol is produced by placing benzene in prolonged contact with air, water, and a hydrocarbon known to give rise to the formation of peroxide of hydrogen by aerial oxidation in the presence of water. A mixture of equal volumes of benzene, water, and Russian turpentine, was heated at  $60^\circ$  in a current of air, for several days, the escaping air being passed through water. The mixture and water soon began to darken, with absorption of oxygen and formation of hydrogen peroxide, but on testing the products for phenol, negative results were obtained, the reactions given being, as far as could be ascertained, those of thymol, and a body resembling pyrogallol.

H. B.

**Dibromo- and Tribromo-orthamidophenetoil and some of their Derivatives.** By R. MÖHLAU and P. OEHMICHEN (*J. pr. Chem.*, **24**, 476—485).—When orthotoluidine mixed with glacial acetic acid is boiled in a flask fitted with reflux condenser, and a quantity of bromine equal to 3 mols. is gradually added while it is still boiling, a mixed product is obtained; with 1 mol. bromine, dibromorthotoluidine

(m. p.  $50^{\circ}$ ) is the chief product; 10 grams orthamidophenetoil and 100 grams glacial acetic acid treated in a similar way with 11.7 grams bromine, give *dibromorthamidophenetoil*,  $C_6H_7Br_2(OEt).NH_2$ , which crystallises from alcohol in tufts of glistening needles (m. p.  $52.5^{\circ}$ ), and dissolves in fuming hydrochloric acid. It distils unchanged. Its constitution is probably  $[OEt : NH_2 : Br : Br] = [1 : 2 : 3 : 5]$ . With 5 grams amidophenetoil, 50 grams acetic acid, 17.5 grams of bromine, *tribromorthamidophenetoil* is produced, which crystallises from alcohol in long silky needles (m. p.  $77^{\circ}$ ), almost insoluble in fuming hydrochloric acid. It decomposes, when heated above its melting point, a bromide of some base subliming, and a bulky coke being left. The authors think this unstability may be due to the fact that one of the bromine-atoms is in the meta-position to the amido-group.

*Dibromodiazophenetoil nitrate*,  $C_6H_7Br_2O.N_2.NO_3$ , is formed when nitrous acid is passed through alcohol containing nitric acid and dibromamidophenetoil, until the latter has disappeared: the product is then poured into pure ether and cooled with ice, when the azonitrate separates out in prismatic needles. It explodes at  $101.5^{\circ}$ . When decomposed by heating with water, we obtain besides some resinous products, a *dibromophenetoil* (probably  $[OEt : Br_2] = [1 : 3 : 5]$ ) an oil (b. p.  $268^{\circ}$ ); it is possible that the reaction may be thus represented:—



In the same way *tribromodiazophenetoil nitrate*, which crystallises in rhombic leaflets, and is prepared by the same method as the dibromoderivative, explodes when struck with a hammer, detonates when heated on platinum foil, and decomposes at  $92^{\circ}$ . On decomposing it with water, it yields a *tribromophenetoil*, which crystallises in dense colourless prisms (m. p.  $72.5^{\circ}$ ), soluble in ether. It is indifferent towards alkalis, and can be distilled without change. Its vapour has a pleasant aromatic odour.

D. A. L.

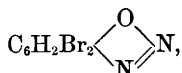
**Preparation of Paranitrophenol Ethers.** By WILLGERODT (*Ber.*, 14, 2632—2638).—On heating paranitrochlorobenzene and potassium hydroxide in molecular proportions with a large excess of methyl alcohol, a dark crystalline mass is obtained, from which, by solution in alcohol and distillation of the extract in a current of steam, *paranitroanisol* can be separated. This compound forms transparent crystals (m. p.  $52^{\circ}$ ) soluble in alcohol. On the sides of the flask, in which the distillation is carried on, crystals of dichlorazoxybenzene (m. p.  $156^{\circ}$ ) are formed.

Similarly, by heating paranitrochlorobenzene, potassium hydroxide, and ethyl alcohol, *paranitrophenetoil* is obtained, together with dichlorazobenzene. The former crystallises in characteristic short thick prisms (m. p.  $59^{\circ}$ ), soluble in alcohol, the latter in long broad golden-yellow needles (m. p.  $185^{\circ}$ ), and is the principal product of the above reaction.

V. H. V.

**Diazophenols.** By C. BÖHMER (*J. pr. Chem.*, 24, 449—475).—The following compounds are described:—*Paradiazophenol hydrochloride* and *nitrate* are best prepared by adding concentrated nitric acid

to an alcoholic solution of paramidophenol hydrochloride and then treating with nitrous acid until, on shaking, small crystals separated out. On cooling, the whole sets to a thick magma of crystals of the nitrate; the hydrochloride remains in the mother-liquor, and is precipitated on the addition of ether. To prepare the *hydrobromide*, an alcoholic solution of paramidophenol hydrobromide is treated with nitrous acid; it is similar in properties to the hydrochloride; the *platinobromide*  $[\text{C}_6\text{H}_4(\text{OH})\text{N}_2\text{Br}]_2\text{PtBr}_4$ , forms brick-red soft needles, which take up 8 mols.  $\text{H}_2\text{O}$  on standing in the mother-liquor, and change to blood-red prisms; it is a very stable body, only slightly soluble in water, and insoluble in ether, chloroform, and carbon bisulphide. It detonates rather violently when heated. By treating an alcoholic solution of amidophenol hydrochloride with dilute sulphuric acid, and then nitrous acid, *diazophenol sulphate* is easily made. This salt does not detonate when heated, but puffs up and leaves a green mass soluble in alcohol. It is, however, easily soluble in alkaline sulphites, giving the yellow colour characteristic of diazo-compounds. When any salt of paradiazophenol is treated with bromine-water, or the nitrate with hydrobromic acid, *paradiazodibromophenol*,



is formed. It is soluble to a small extent in most solvents, and from amyl alcohol it crystallises in flat spearheads, from water in yellow prisms. By exposure to light, it soon becomes discoloured, but not in the dark; it is very stable, not being decomposed even if boiled with water. When heated to  $137^\circ$  it detonates, leaving a grey bulky mass containing bromine, and insoluble in acids, alkalis, and all ordinary solvents. Paradiazodibromophenol shows slightly basic properties, and forms salts. The *hydrobromide*,  $\text{C}_6\text{H}_2\text{Br}_2(\text{OH})\text{N}_2\text{Br} + \text{H}_2\text{O}$ , crystallises from fuming hydrobromic acid in pale reddish glittering needles; it is easily decomposed into the base and acid by water or alcohol. The *platinochloride*,  $[\text{C}_6\text{H}_2\text{Br}_2(\text{OH})\text{N}_2\text{Br}]_2\text{PtCl}_4$ , crystallises in red-yellow leaflets with golden lustre; under the microscope they appear to be rhombic tablets. The dry salt is very stable; heated quickly it detonates, but if gradually, it burns quietly. The *sulphate*,

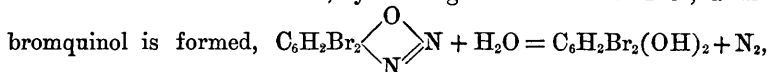


forms small soft pale-red needles, decomposable by water.

Orthodiazophenol derivatives are prepared in the same way as the para-derivatives. *Orthodiazodibromophenol* is the product of the action of bromine on these derivatives; it forms orange-red crystals more sensitive to chemical reagents than the corresponding para-compound. It is soluble in cold water, and becomes resinous in warm water; silver nitrate gives a grey amorphous precipitate with the aqueous solution. Alcohol, ether, and carbon bisulphide dissolve it sparingly, whilst chloroform, petroleum, hot benzene, and fuming hydrochloric acid dissolve it readily. It appears to be converted into a hydrazine by reducing agents. The *hydrobromide* is similar in properties to the salt of the para-derivative; it crystallises in small yellow needles with  $1\frac{1}{2}$  mols.



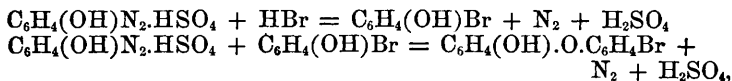
H<sub>2</sub>O. The following reactions prove that these bodies produced by direct bromination are really diazo-compounds. When digested with amyl alcohol at 130°, paradiazodibromophenol gives off part of its nitrogen with the production of an amorphous substance soluble in alkalis. On the other hand, by heating with water at 125°, a di-



which, on oxidation, yielded a dibromquinone volatile in water vapour.

By treating the diazobromophenol with acid sodium sulphite, *sodium paradiazodibromophenolsulphonate*,  $\text{C}_6\text{H}_2\text{Br}_2\text{N}_2(\text{OH}).\text{SO}_3\text{Na} + 2\text{H}_2\text{O}$ , is formed. It crystallises in small yellow needles easily soluble in water, ether, benzene, carbon bisulphide, and boiling alcohol, sparingly in cold alcohol; deliquesces on the surface when exposed to the air, becoming grey in colour; loses water at 100°, and does not detonate on heating. It neither reduces metallic oxides nor Fehling's solution; but shows Liebermann's reaction for diazo-bodies. *Barium paradiazodibromophenolsulphonate*,  $[\text{C}_6\text{H}_2\text{Br}_2\text{N}_2(\text{OH}).\text{SO}_3]_2\text{Ba} + 5\text{H}_2\text{O}$ , forms golden-yellow scales only slightly soluble in water and alcohol, insoluble in ether, &c. Shows reactions for diazo-body. *Silver paradiazodibromophenolsulphonate* crystallises in tufts of yellow needles, which appear to be united at the top in pairs. Paradiazodibromophenol when reduced with tin and hydrochloric acid, gives rise to *para-amidodibromophenol*,  $\text{C}_6\text{H}_2\text{Br}_2(\text{OH}).\text{NH}_2$ , a precipitate of tufts of microscopic needles, which dissolve sparingly in ether, easily in alcohol, turn blue in the air, and melt at about 178°. *The hydrochloride* crystallises in glittering colourless tables, easily soluble in acidulated water and alcohol. *The diazodibromophenol* made by treating this amidodibromophenol with nitrous acid crystallises in dark greyish-yellow needles, insoluble in water and ether, very sparingly in cold alcohol, carbon bisulphide, and benzene, easily in boiling alcohol and amyl alcohol, from which solution it crystallises in small needles. It evaporates at 145°; it hence differs from the above-described paradiazodibromophenol. The author then sums up the facts, and concludes therefrom that these brominated bodies are substitution-products of the diazophenols.

As hydrobromic acid gave rise to a very characteristic reaction with diazophenol nitrate, the author has studied its action on other salts of diazophenol. When the sulphate, for instance, is digested in a water-bath with this acid, an oil separates out which, after distilling with steam and fractionating and otherwise purifying, gave numbers on analysis agreeing with *bromophenylphenol ether*,  $\text{C}_6\text{H}_4\text{Br}.O.C_6\text{H}_4.OH$ ; the reaction takes place in two stages thus:—



This ether is colourless, is not miscible with water, but dissolves easily in alcohol, ether, and alkalis, from which solution it is reprecipitated by acids. Its odour is extremely penetrating and persistent. Dilute nitric acid reacts violently on it. On distillation, a yellow solid

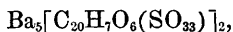
body is formed containing bromine, and melting under but only sparingly soluble in hot water. D. A. L.

**Resorcinoxaleïn.** By A. CLAUS (*Ber.*, **14**, 2563—2570).—The author proposes the name *resorcinoxaleïn* for the compound previously described (*Ber.*, **10**, 1305) as diresorcinketone, and formed by heating a mixture of oxalic acid and resorcinol in molecular proportions at 200° in sealed tubes. The *oxaleïn*,  $\text{OH.C}_6\text{H}_3 < \text{CO} > \text{C}[\text{C}_6\text{H}_3(\text{OH})_2]_2$ , is deposited from an alcoholic solution as a red powder, which is soluble in ether. When this substance is heated at 150°, it loses a molecule of water; the residue is insoluble in ether, and is less soluble in alcohol than the hydrate. The *oxaleïn* dissolves in concentrated potash-lye, forming a blue solution; if solid potash is added, and the mixture gently fused until the mass acquires a yellow colour, the *resorcinoxaleïn* is split up into resorcinol and oxalic acid.

*Diacetic oxaleïn*,  $\text{C}_{20}\text{H}_{10}\text{O}_6\text{Ac}_2$ , is a yellowish-red body formed by boiling *oxaleïn* with acetic anhydride. If the operation is conducted in sealed tubes at 150°, the colourless triacetic derivative is produced.

*Pentabromoxaleïn*,  $\text{C}_{20}\text{H}_7\text{Br}_5\text{O}_6$ , prepared by boiling the *oxaleïn* with a large excess of bromine, is a dark-red powder, which decomposes at 230° without melting. It unites with metallic oxides, forming salts. Fuming nitric acid converts *resorcinoxaleïn* into trinitroresorcinol and oxalic acid. By the action of strong nitric acid on an acetic acid solution of the *oxaleïn*, a tetranitroxaleïn,  $\text{C}_{20}\text{H}_5\text{O}_6(\text{NO}_2)_4$ , is produced. It is a dark-red substance, which decomposes at 200° without melting.

The *oxaleïn* dissolves in strong sulphuric acid with an emerald coloration. If the liquid is heated at 110°, its colour changes to red, owing to the formation of a sulphonic acid,  $\text{C}_{20}\text{H}_9\text{O}_6(\text{SO}_3\text{H})_3$ . The acid forms very deliquescent crystals. The barium salt,



is a red crystalline powder soluble in water. When an aqueous solution of the acid is boiled with excess of baryta, an insoluble salt of the composition,  $\text{Ba}_4\text{C}_{20}\text{H}_5\text{O}_7(\text{SO}_3)_3$ , is precipitated. W. C. W.

**Resorcintartreïn and Resorcincitreïn.** By G. FRAUDE (*Ber.*, **14**, 2558—2559).—*Resorcintartreïn* is prepared by heating a mixture of resorcinol (2 mols.) and tartaric acid (1 mol.) with 1 per cent. of sulphuric acid or zinc chloride for two hours at 165°. The tarry product is dissolved in warm soda-lye, and the filtered liquid is acidified with hydrochloric acid. The precipitate is dried, dissolved in alcohol, treated with animal charcoal and precipitated by water. It forms an olive-green powder soluble in ammonia, alkaline carbonates, and in potash or soda-lye. These solutions are strongly fluorescent. The substance unites with bromine to form a compound which dissolves in alkaline carbonates, yielding a beautiful carmine solution.

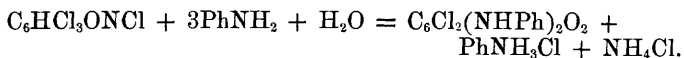
If citric acid is substituted for tartaric acid, an analogous compound

is obtained. Like the tartrein, it dissolves in alkalis, forming a deep red liquid, which exhibits an intense blue fluorescence.

W. C. W.

**Dibromoquinol.** By E. SARAUF (*Ber.*, **14**, 2539—2540).—A reply to Benedikt (*Ber.*, **14**, 2121).

**Trichloroquinone Chlorimide.** By R. SCHMITT and M. ANDRESEN (*J. pr. Chem.* [2], **24**, 426—443).—The preparation of trichloropar- amidophenol and its conversion into trichloroquinone chlorimide by the action of bleaching powder has been already described (*J. pr. Chem.* [2], **23**, 435). Ammonia and the amines of the fatty series do not yield uniform products by their action on an alcoholic solution of trichloroquinone chlorimide; the results with aromatic amines are, however, more satisfactory. Thus aniline reacts to form *dichloroquinone-dianilide*; its formation is explained as follows:—



*Dichloroquinone dianilide*,  $\text{C}_6\text{Cl}_2(\text{NHPh})_2\text{O}_2$ , crystallises from benzene in yellowish-brown prismatic leaflets, having a metallic lustre; it is insoluble in water, and only sparingly soluble in alcohol and ether; it dissolves in concentrated sulphuric acid, forming a deep blue solution.

*Dichloroquinone diorthethoxyanilide*,  $\text{C}_6\text{Cl}_2(\text{NH.C}_6\text{H}_4.\text{OEt})_2\text{O}_2$ , is obtained in a similar manner by substituting orthamidopheneticol for aniline. It is obtained in long brown shining prisms by cooling its hot alcoholic solution (m. p.  $200^\circ$ ); it is insoluble in water, and is precipitated by it from its alcoholic solution in light green crystals. Alkalis and dilute acids do not decompose it, but concentrated sulphuric acid dissolves it, forming a blue solution.

Accepting the above reactions as typical of the action of amines on trichloroquinone chlorimide, the authors conclude that there can be but one dichloroquinone dianilide, and therefore the one described above must be identical with that obtained by Hesse by the action of aniline on tetrachloroquinone; further, that trichloroquinone and aniline should yield a dichloroquinone dianilide and not a monochloro-dianilide, as stated by Schultz and Neuhöffer (*Ber.*, **10**, 1792). The accuracy of this last conclusion the authors have confirmed by experiment.

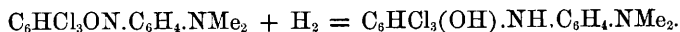
*Trichloroquinone dimethylanilide*,  $\text{C}_6\text{HCl}_3\text{ON.C}_6\text{H}_4.\text{NMe}_2$ , is obtained by acting on an alcoholic solution of trichloroquinone chlorimide with dimethylaniline; its formation is explained as follows:—



Its formation is attended by the production of a dark-blue colour, which may be utilised to indicate the presence of one or other of these substances. The substituted anilide crystallises from alcohol in dark, lustrous, elastic and ductile needles, having a blue streak; it is insoluble in water but soluble in ether, benzene, and chloroform, and imparts a blue colour to silk. Like quinonechlorimide it is converted into a

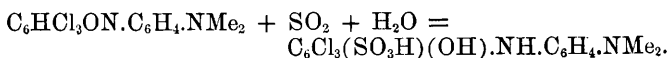
phenol by reducing agents, *e.g.*, ammonium sulphide, and if sulphurous anhydride is used, a sulphonic acid is obtained.

*Trichlorodimethylaniline amidophenol*,  $\text{C}_6\text{HCl}_3(\text{OH})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ , is insoluble in water, but is easily soluble in other solvents; its formation is explained by the following equation:—



As a phenol, it forms salts with bases, which are unstable and easily reconverted into the chlorimide by exposure to the air; it also possesses basic properties, and forms crystalline salts with acids; the chloride and sulphate are sparingly soluble in water.

*Trichlorodimethylaniline Amidophenolsulphonic Acid*.—Its formation is expressed by the following equation:—



The above phenol is formed simultaneously, and the sulphonic acid is separated from it by treatment with ammonia. The ammoniacal solution when treated with hydrochloric acid, yields a white crystalline precipitate of the sulphonic acid, which is insoluble in ordinary solvents, but soluble in concentrated sulphuric acid. P. P. B.

**Absorption of Oxygen by Alkaline Solutions of Pyrogallol and Phloroglucol.** By T. WEYL and A. GOTH (*Ber.*, **14**, 2659—2674).—One of the authors, in association with Zeilter, has shown that the absorptive power of the potash solution of pyrogallol is a function of the alkalinity of the solution (Abstracts, 1881, 308); in the present communication, experiments are made with a view of ascertaining whether the absorption is dependent on the presence of a definite alkali, or generally of any alkali; and secondly, whether by the action of alkalis on pyrogallol a compound is formed, to which the absorptive power must be referred. Experiments are quoted to show that the absorption power reaches its maximum when sufficient soda is taken to form the compound  $\text{C}_6\text{H}_3(\text{ONa})_3$ , but this is not the case when potash is substituted for soda, and is a direct contradiction to the experiments of Pelouze, which showed that the sodium and potassium compounds of pyrogallol are formed only in absence of air. It has already been shown that carbonic anhydride is produced by the action of air on alkaline pyrogallate, and determinations of the quantity so produced are quoted. Attention is also drawn to a statement in *Gmelin's Handbook*, that pyrogallol decomposes the alkaline carbonates; this the authors consider to be due to the formation of acetic acid, which is slowly produced by the action of oxygen on pyrogallol. With sodium or potassium hydroxide or sodium carbonate, the absorptive power is equally a function of the alkalinity of the solution. Phloroglucol, like pyrogallol, absorbs oxygen, but to a less degree; the authors propose to examine further its absorptive power.

V. H. V.

**Nitration of Paranitrocinnamic Acid.** By P. FRIEDLÄNDER (*Ber.*, **14**, 2575—2577).—If ethyl paranitrocinnamate is slowly added

to a mixture of strong sulphuric acid (6 parts) and nitric acid (50° B.) (3 parts), nitration takes place in the side-chain of the etheric salt. The acid solution is poured into water, and after several hours the liquid is extracted with ether. The extract is then shaken with soda, and evaporated, when pale-yellow plates (m. p. 110°) are deposited. This compound,  $C_{11}H_{10}N_2O_6$ , is soluble in alcohol, ether, and benzene. Methyl paranitrocinnamate under similar treatment yields white needles (m. p. 104°). Paranitrocinnamic acid also forms a nitro-product (m. p. 196°), which is deposited from acetone in needle-shaped crystals. By oxidation with a solution of chromic acid in glacial acetic acid, these compounds are converted into paranitrobenzoic acid. If a less energetic oxidising agent is employed, paranitrobenzaldehyde is obtained. It is identical with the aldehyde which Fischer and Grieff (*Ber.*, 13, 669) obtained from paranitrobenzyl chloride.

W. C. W.

**Opianic Acid.** By O. PRINZ (*J. pr. Chem.* [2], 24, 353—374).—Opianic acid is purified by passing a current of nitrogen trioxide through its hot aqueous solution; on cooling the filtered solution, the acid separates out in almost white crystals, which can be obtained perfectly colourless by treating them with a little potassium permanganate and sulphuric acid. Nitrous acid does not act on opianic acid; dilute nitric acid oxidises it slowly to hemipinic acid, and concentrated nitric acid converts it into a mixture of nitro-opianic and nitro-hemipinic acids, and a small quantity of a substance having the composition  $C_{10}H_{10}NO_6$ .

*Nitro-opianic acid*,  $CHO.C_6H(NO_2)(OMe)_2.COOH$ , is separated from the above by its insolubility in cold water; it crystallises in pale yellow shining prisms, m. p. 166°. Its salts are easily soluble in water.

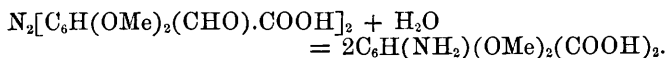
*Barium nitro-opianate*,  $(C_{10}H_8NO_7)_2Ba + 3H_2O$ , crystallises in large yellow needles; *potassium nitro-opianate*,  $C_{10}H_8NO_7K + 3H_2O$ , forms thick transparent prisms; the sodium salt crystallises in long deep yellow prisms. *Ethyl nitro-opianate*,  $C_{10}H_8NO_7$ , crystallises from carbon bisulphide in beautiful needles, it is soluble in alcohol, ether, and hot benzene, m. p. 96°. When melted under water it is resolved into the acid and alcohol.

*Nitro-hemipinic acid*,  $C_6H(NO_2)(OMe)_2(COOH)_2 + H_2O$ , is obtained from the mother-liquors of nitro-opianic acid, or better by heating equal weights of opianic acid and nitric acid until the evolution of red fumes ceases. The nitro-hemipinic acid is separated from the nitro-opianic acid by the insolubility of its barium salt in water. The acid obtained by decomposing the barium salt with sulphuric acid crystallises in hard, vitreous, monoclinic prisms, containing water of crystallisation; when anhydrous it melts at 155°. Nitro-hemipinic acid is not obtained by oxidising nitro-opianic acid with nitric acid. Its salts, with the exception of the lead and barium salt, are insoluble in water.

*Barium nitro-hemipinate*,  $C_{10}H_7NO_8Ba + 2\frac{1}{2}H_2O$ , is obtained as a white crystalline precipitate by adding barium chloride to the ammoniacal solution of the acid; the crystals effloresce.

*Azo-opianic acid*,  $C_{20}H_{18}N_2O_{10}$ , is obtained by reducing nitro-opianic

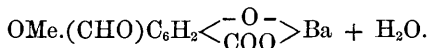
acid with stannous chloride and hydrochloric acid; on cooling, it separates as a voluminous precipitate of white needles. Ammonium sulphide reduces nitro-opianic acid in a similar manner, but tin and hydrochloric acid do not give satisfactory results. Azo-opianic acid dissolves in alkalis, and forms unstable compounds with acids; its hydrochloride loses hydrochloric acid when dried over lime or sulphuric acid. *Barium azo-opianate*,  $\text{N}_2[\text{C}_6\text{H}(\text{OMe})_2(\text{CHO}).\text{COO}]_2\text{Ba} + 6\text{H}_2\text{O}$ , is obtained by dissolving the acid in baryta-water and removing excess of barium by means of carbonic anhydride; it forms fine silky needles. When boiled with baryta-water a golden-yellow precipitate is formed, which appears to be *barium amido-hemipinate*; its formation is explained as follows:—



*Monochloro-opianic acid*,  $\text{C}_{10}\text{H}_9\text{ClO}_6$ , is obtained by acting on opianic acid with hydrochloric acid and potassium chlorate; it crystallises from water in brilliant small needles, m. p. 210—211°. Its salts, except those of the alkali-metals, are sparingly soluble in water. A dichloro-acid appears to be formed by the further action of hydrochloric acid and potassium chlorate.

Bromine reacts on opianic acid, forming substitution-products.

*Methylnoropianic acid*,  $\text{C}_6\text{H}_2(\text{OMe})(\text{OH})(\text{CHO}).\text{COOH}$ , is prepared, as described by Matthiesen and Foster (this Journal [2], 6, 387), by the action of hydrochloric acid on opianic acid. To purify the acid from unaltered opianic acid, the product is neutralised with ammonia, and barium chloride added; the filtrate from the precipitated barium opianate is treated with more barium chloride and made strongly alkaline with ammonia; in this way, a green gelatinous precipitate of barium methylnoropianate is obtained, which yields the free acid when decomposed by sulphuric acid. The barium salt becomes crystalline on standing, and has the composition—



*Monochloromethylnoropianic acid*,  $\text{C}_6\text{HCl}(\text{OMe})(\text{OH})(\text{CHO}).\text{COOH}$ , is obtained by the action of potassium chlorate and hydrochloric acid on methylnoropianic acid. Crystallised from hot water, it forms large shining needles, m. p. 206°. Chloranil is obtained by the further action of hydrochloric acid and potassium chlorate on chloromethylnoropianic acid.

Phosphorus pentachloride reacts with hemipinic acid, forming hemipinic anhydride, m. p. 167° (v. Matthiesen and Foster, *loc. cit.*). Phosphorus pentachloride reacts with opianic acid to form a chloride, which has not been isolated; its ethereal solution when treated with zinc and hydrochloric acid yields meconin, and not opianic aldehyde.

P. P. B.

**Benzyloxyphenylacetic and Paramethylbenzyloxyphenylacetic Acids.** By G. MAZZARA (*Gazzetta*, 11, 437—439).—*Benzyloxyphenylacetic acid*,  $\text{CH}_2\text{Ph}.\text{C}_6\text{H}_4.\text{O}.\text{CH}_2.\text{COOH}$ , is prepared by heating benzylphenol with monochloroacetic acid, and then adding potash solu-

tion and heating again. When cold, the product is diluted with water, acidified with hydrochloric acid, and then rendered alkaline by ammonium carbonate; this dissolves the acid, and leaves the unaltered phenol which is removed, and the acid is precipitated by hydrochloric acid. Purified by crystallisation from dilute alcohol, it forms small colourless odourless needles (m. p.  $100^{\circ}$ ), easily soluble in alcohol and ether, sparingly soluble in water.

*Paramethylbenzyl-oxyphenylacetic acid*,



is prepared in a similar manner to the above, and like it crystallises in small, white, tasteless, and odourless needles (m. p.  $109-111^{\circ}$ ).

The author has prepared the barium salts of these acids; they crystallise in white plates, but the quantity was too small for analysis.

C. E. G.

**Some Derivatives of Phthalic Acid.** By O. MILLER (*Annalen*, **208**, 223—248).—According to theory, two isomeric monoderivatives of phthalic acid are possible; both nitro-derivatives corresponding with these are known: the ordinary or  $\alpha$ -acid, obtained from  $\alpha$ -nitronaphthalene, and the other or  $\beta$ -acid described by the author. Faust (*Annalen*, **160**, 56) has described the preparation of these isomerides by the nitration of phthalic acid; but the author prefers using rather more nitric and sulphuric acids. The mixed nitro-acids, precipitated by water, are extracted by ether, evaporated to dryness, and the  $\alpha$ -acid separated by crystallisation from water; the mother-liquor containing the  $\beta$ -acid and some picric acid is evaporated to dryness, and its alcoholic solution treated with dry hydrochloric acid on the water-bath. By this means the  $\beta$ -acid is converted into ethyl  $\beta$ -nitrophthalate, and the  $\alpha$ -acid present into ethyl hydrogen  $\alpha$ -nitrophthalate. The ethyl salt is precipitated by water, treated with soda-solution to remove the  $\alpha$ -salt and yellow colouring matters, and finally crystallised from ether. The  $\beta$ -acid is obtained by saponifying the ethyl salt and decomposing the colourless potassium salt by hydrochloric acid. The  $\beta$ -acid dissolves almost equally well in water, alcohol, and ether, but it is practically insoluble in benzene and chloroform. The water of crystallisation cannot be estimated on account of rapid efflorescence. The dry acid melts at  $161^{\circ}$  to a transparent yellow liquid, and solidifies at  $118-119^{\circ}$ ; above  $165^{\circ}$  the anhydride (m. p.  $114^{\circ}$ ) is formed, volatile in a current of air at  $210^{\circ}$ ; it is almost colourless, and is only sparingly soluble in cold, but more readily in hot water, and in ether. The potassium, silver, barium, and zinc salts are described.

Ethyl-hydrogen  $\beta$ -nitrophthalate is formed in traces in making the neutral ethyl salt.

$\beta$ -Nitrophthalic acid is reduced by tin and hydrochloric acid to  $\beta$ -amidophthalic acid, decomposing on evaporation into carbonic anhydride and [1 : 3] amidobenzoic acid.

The  $\alpha$ -acid has been said to melt at  $208-210^{\circ}$ ; the author, however, states that no proper fusion takes place, but that the acid decomposes into its anhydride and water, at or even under  $210^{\circ}$ , a small quantity of a liquid substance, a solution of the acid in the anhydride, remains, which, after solidification, melts at about  $160^{\circ}$ . The acid

heated in a capillary tube closed just above the substance, melts at  $218^{\circ}$ . The silver, zinc, and barium salts of the  $\alpha$ -acid are described.

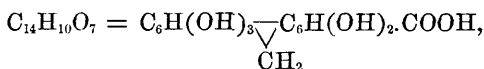
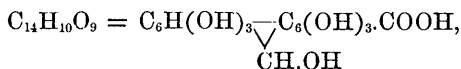
In reducing  $\alpha$ -nitrophthalic acid by tin and hydrochloric acid, the author finds, contrary to Faust, that no carbonic anhydride is evolved. The product,  $C_6H_3(NH_2HCl)(COOH)_2, SnCl_4, 2H_2O$  (calculated from a chlorine determination) crystallises out during the reaction; its hydrochloric acid solution, like that of the  $\beta$ -acid, when treated with sulphuretted hydrogen, and evaporated, yields [1 : 3] amidobenzoic hydrochloride.

Ethyl  $\alpha$ -amidophthalate, obtained by reducing ethyl  $\alpha$ -nitrophthalate with zinc and hydrochloric acid in alcoholic solution, is an odourless yellow oil, which becomes brown in the air, and cannot be distilled without decomposition. Its highly diluted ethereal solution shows a fine blue fluorescence.

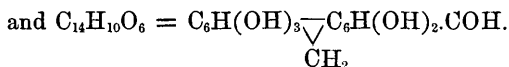
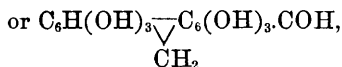
Ethyl  $\alpha$ -hydroxyphthalate, obtained by the action of potassium nitrite on ethylamidophthalate dissolved in sulphuric acid, is a brown oil, which on being saponified and adding an acid, yields to ether a brown mass containing  $\alpha$ -hydroxyphthalic acid. This acid, after purification, is readily soluble in water, alcohol, and ether. Ferric chloride colours it intensely cherry-red. Its silver salt is sparingly soluble. This acid is also obtained by oxidising acetyl- $\alpha$ -naphthol in acetic acid by chromic acid.

F. L. T.

**Action of Nascent Hydrogen on Ellagic Acid.** By A. COBENZL (*Monatsh. Chem.*, **1**, 670—674).—By treating ellagic acid with an equal quantity of sodium (as 4 per cent. amalgam) for three hours, a substance,  $C_{14}H_{10}O_7$ , is obtained, crystallising in silky yellow needles and giving a fine blue coloration with ferrous sulphate. When the action of sodium is continued for 24 hours, two substances are obtained soluble in ether, of which the one more soluble in cold water (previously obtained in an impure state by Rembold, this *Journal*, 1876 [1], 592) has the formula  $C_{14}H_{10}O_6$ , and sublimes in brilliant golden-yellow needles. The less soluble compound,  $C_{14}H_{10}O_9$ , crystallises in white needles. Both bodies give a wine-red coloration with ferric chloride, turning green on addition of sodium carbonate; they have an acid reaction, and can be dried at  $100^{\circ}$ . By employing double the weight of sodium and continuing the action for 48 hours, the  $\gamma$ -hexahydroxydiphenyl of Barth and Goldschmidt (*Abstr.*, 1879, 930) was obtained. This melts at  $70^{\circ}$ , and its acetyl derivative crystallises in colourless tables (m. p.  $163$ — $164^{\circ}$ ). In all cases these products were obtained in small quantity (2—3 per cent.). The author suggests the following constitutional formulæ for these bodies:—







A. J. G.

**Compounds formed in the Electrolysis of various Liquids by Means of Carbon Electrodes.** By A. BARTOLI and G. PAPA-SOGLI (*Gazzetta*, **11**, 468—479).—When a powerful electric current is passed between carbon electrodes immersed in an acid solution, the electrodes become disintegrated, and a black deposit is produced consisting of unaltered carbon mixed with a black compound which the authors call *Mellogen* or *Mellitogen*; this is an amorphous solid which can be pulverised with facility; it is insoluble in nearly all neutral solvents with the exception of water. In this it is but sparingly soluble when cold, but more readily when hot; the solution is precipitated by acids and by salts. It is soluble in alkaline solutions and in concentrated sulphuric acid, but is precipitated from the latter on adding water. Its density is about 1·7, and it adheres readily to vegetable fibres. Although carbon electrodes become rapidly disintegrated in alkaline solutions, the deposit contains but little mellogen.

The most salient property of mellogen is the readiness with which it combines with oxygen to form mellic acid or its derivatives, a property which sharply distinguishes it from the ulmic compounds so closely resembling it in appearance. Its aqueous solution slowly becomes acid on exposure to the air, and when the substance itself is treated with an alkaline hypochlorite, heat is developed, carbonic anhydride is evolved, and benzenecarboxylic acids are formed. These may be separated by adding barium nitrate to the filtered solution; the precipitated barium salts are converted into the corresponding sodium compounds, and the mellic acid precipitated as calcium mellate; the mellic acid was recognised by analysis in the free state and as silver salt, and by the action of heat on the ammonia salt, producing paramide and eucronic acid. The readiness with which mellogen is oxidised to mellic acid explains the fact that the dark solution produced in the electrolysis of alkaline solutions by carbon electrodes contains abundance of benzenecarboxylic compounds and but little mellogen, whilst in acid solutions the reverse is the case: the mellogen, being soluble in alkaline solutions, is readily oxidised by the oxygen evolved at the positive pole, whilst in acid solutions it remains insoluble, and escapes oxidation.

With regard to the gaseous products obtained with carbon electrodes, the authors find that hydrogen is disengaged at the negative pole, and carbonic oxide and anhydride with a little oxygen at the positive pole, the volume of hydrogen being sensibly equal to that obtained in a voltameter included in the circuit; but the gas evolved at the positive pole is very small in proportion to the hydrogen at the negative pole, although this proportion increases with the absolute intensity of the current.

The electrolysis of alcohol rendered slightly alkaline gave aldehyde

and its polymerides with a little acetic acid and aldehyde-resin, the carbon electrodes being but slightly disintegrated, and but little deposit formed. With dilute alkaline glycerol, on the contrary, the electrodes are greatly disintegrated, and a deposit containing much mellogen is formed, whilst acetaldehyde, acrylic acid, and a semi-solid acid compound are found in solution. Acidified glycerol gave the same compounds in smaller quantity, but the carbonaceous deposit was larger and contained a larger proportion of mellogen.

Phenol in alkaline solution is readily attacked, the liquid becoming almost black, and an abundant black deposit produced. The filtered solution gives a copious precipitate of a dark chestnut colour when acidified with hydrochloric acid. This substance appears to be allied to the glucosides. It is insoluble in ether, sparingly in hot water, but soluble in acetone and in alcohol, yielding a dark-red solution. It is also very soluble in alkaline solutions. When boiled for some hours with dilute hydrochloric acid, it splits up into two compounds: one black and insoluble in alcohol and ether; the other a dark-red, transparent, amorphous substance (m. p.  $60^{\circ}$ ), easily soluble in boiling water, but only sparingly in the cold. It is very soluble in ether, and readily reduces Fehling's solution. Besides these two compounds, another has been extracted from the first hydrochloric acid solution. It is crystalline (m. p.  $93^{\circ}$ ), soluble in water, alcohol, and ether, yielding fluorescent solutions. Its ammonium salt crystallises in beautiful needles.

C. E. G.

**Phenolorthosulphonic Acid.** By J. HERZIG (*Monatsh. Chem.*, **1**, 664—669).—The potassium salt of this acid can be obtained in well defined crystals, with 2 mols.  $H_2O$ ; the salt with a varying percentage of water usually obtained appears to be a mixture of the above with an anhydrous salt. When fused with potash, the potassium salt yields catechol and a small quantity of a diphenol, apparently identical with that obtained by Linke from phenolparasulphonic acid. This diphenol probably owes its formation to the transformation by heat of a portion of the ortho- into the para-salt.

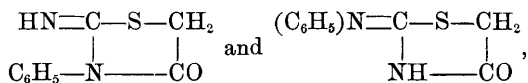
A. J. G.

### Synthesis of Thiohydantoins by Means of Thioglycollic Acid.

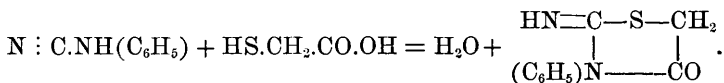
By R. ANDREASCH (*Monatsh. Chem.*, **2**, 775—781).—The author showed in a former paper (*Ber.*, **13**, 1421) that cyanamide unites with thioglycollic acid to form thiohydantoin; and the following experiments, made, on the one hand, with substituted cyanamides, and on the other with substituted thioglycollic acids, show that this reaction is capable of general application.

1. *Action of Phenylcyanamide on Thioglycollic Acid: Synthesis of Phenylthiohydantoin.*—An alcoholic solution of phenylcyanamide, obtained by desulphurising the corresponding phenylthiocarbamide with lead oxide, was left at rest for a few days, then freed from about two-thirds of the alcohol by distillation, and the residual dark brown liquid was left for some time in a cool place, whereupon it deposited small crystalline nodules, which were easily separated from adhering thioglycollic acid by boiling with a little water. After boiling with soda-lye, but not before, they exhibited the iron reaction of thioglycollic acid,

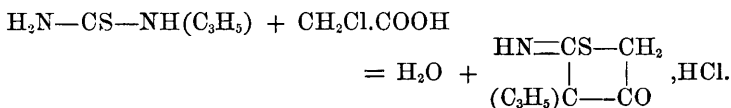
showing that they really consisted of a thiohydantoin, inasmuch as the separation of thioglycollic acid on heating with bases is characteristic of these bodies. On triturating the crystalline nodules with a small quantity of soda-lye, the entire mass was converted into a pulp of shining scales; and on dissolving these in water, and passing carbonic anhydride through the solution, a reddish-yellow precipitate was obtained, consisting of microscopic needles, and forming, after recrystallisation from boiling alcohol, shining, faintly yellowish prisms, agreeing in melting point ( $178^{\circ}$ ) with the phenyl-thiohydantoin which P. J. Meyer obtained from chloracetanilide and thiocarbamide. Now of the two possible formulæ of a phenylthiohydantoin, viz.,



the first only can belong to a body obtained by the reaction last mentioned: hence it follows that the reaction between phenylcyanamide and thioglycollic acid must be represented by the equation—



2. *Allyl-thiohydantoins*.—Bodies of this composition have been obtained by the author in two ways:—(1.) By the ordinary method of preparing thiohydantoins, viz., by the action of monochloroacetic acid on allylthiocarbamide, the immediate product being a hydrochloride of the thiohydantoin—



On treating the solution of this hydrochloride with recently precipitated silver oxide, silver chloride is precipitated, and the filtrate, on evaporation, deposits whitish mostly amorphous crusts of free allylthiohydantoin.

This allylthiohydantoin dissolves sparingly in cold water and alcohol, easily in hot water, forming a neutral solution, which, when mixed with hydrochloric acid and evaporated, deposits the characteristic needle-shaped crystals of the hydrochloride. After boiling the body with an alkali, it gives with ferric chloride the red coloration of thioglycollic acid.

3. The same allylthiohydantoin is obtained by the action of thioglycollic acid on allylcyanamide. An aqueous solution of thiocyanamide was mixed with well washed levigated mercuric oxide, till a drop of the liquid tested on filter-paper with silver nitrate no longer gave a black spot of silver sulphide; and the filtrate, containing allylcyanamide, was mixed with a quantity of thioglycollic acid, equal in weight to the allylthiocarbamide used. On leaving the liquid to itself for

some time, then boiling and evaporating it over the water-bath, mixing the residual syrup with dilute hydrochloric acid, again evaporating, and leaving the remaining liquid in a cold place, the whole solidified to a thick crystalline pulp, which could easily be freed from the syrupy mother-liquor by recrystallisation from warm water. In this manner, slender needles were obtained, agreeing exactly in appearance and solubility with the allylthiohydantoin prepared by the first method. The reaction between allylcyanamide and thioglycollic acid takes place in the same manner as that between the same acid and phenylcyanamide. It must be observed, however, that the yield of thiohydantoins by this method is small in comparison with that which is obtained by the ordinary method of preparing the same compounds.

H. W.

**Action of Mercuric Ethide on Iodides.** By W. SUIDA (*Monatsh. Chem.*, **1**, 713—723).—When allyl iodide is heated with mercuric ethide in sealed tubes at 120—150° for two days, it yields ethyl iodide, diallyl, and mercuric ethiodide, no bye-products being observed. When mercuric phenylide was employed, diphenyl was formed, as well as diallyl, the reaction being expressed by  $2\text{HgPh}_2 + 2\text{C}_3\text{H}_5\text{I} = \text{C}_6\text{H}_{10} + 2\text{HgPhI} + \text{C}_{12}\text{H}_{10}$ . On slowly heating equal weights of mercuric ethide and iodoform at 120° in sealed tubes, the products obtained are mercuric ethiodide, ethyl iodide, ethylene, and acetylene. A. J. G.

**Derivatives of  $\delta$ - and  $\epsilon$ -Dichloronaphthalene.** By J. E. ALÉN (*Bull. Soc. Chim.* [2], **36**, 433—436).—When  $\delta$ -dichloronaphthalene (m. p. 114°) is heated with nitric acid in sealed tubes at 140° (sp. gr. 1.21), it yields a monochlorophthalic acid,  $\text{C}_6\text{H}_3\text{Cl}(\text{COOH})_2$ , showing that the  $\delta$ -compound contains 1 atom of chlorine in each benzene nucleus. On treating  $\delta$ -dichloronaphthalene for a week with concentrated nitric acid, a mixture of two mononitrodichloronaphthalenes is obtained. One of these melts at 141.5—142°; the other has not been obtained quite free from dichloronaphthalene, but its melting point is about 95°. Both crystallise in needles, which become green on exposure to the air. By dissolving  $\delta$ -dichloronaphthalene in glacial acetic acid, adding fuming nitric acid, and heating the mixture for a few minutes, a dinitro-compound,  $\text{C}_{10}\text{H}_4\text{Cl}_2(\text{NO}_2)_2$ , is obtained. It forms pale-yellow prisms (m. p. 245—246°), which become green in the air. By boiling  $\delta$ -dichloronaphthalene with fuming nitric acid, a trinitro-derivative is obtained,  $\text{C}_{10}\text{H}_3\text{Cl}_2(\text{NO}_2)_3$ , crystallising in pale-yellow needles (m. p. 200—201°).

By heating  $\epsilon$ -dichloronaphthalene (m. p. 135°) with nitric acid of sp. gr. 1.21, a mixture of monochlorophthalic acid and nitromonochlorophthalic acid is obtained. On subliming, the anhydride  $\text{C}_6\text{H}_3\text{Cl}(\text{CO})_2\text{O}$  of the former is obtained, crystallising in colourless needles (m. p. 95°). The  $\epsilon$ -modification, therefore, contains 1 atom of chlorine in each benzene nucleus. By acting on  $\epsilon$ -dichloronaphthalene with concentrated nitric acid at a low heat, two modifications of mononitrodichloronaphthalene are obtained, crystallising in yellowish needles, which change to brownish-violet in the air. One melts at 113.5—114°, the other at 139—139.5°. Fuming nitric acid yields a dinitro-compound (m. p. 252—253°),  $\text{C}_{10}\text{H}_4\text{Cl}_2(\text{NO}_2)_2$ . On boiling with fuming nitric

acid, trinitrodichloronaphthalene,  $C_{10}H_3Cl_2(NO_2)_3$ , is formed, crystallising in pale-yellow needles (m. p. 198—200°). By acting on  $\epsilon$ -dinitrodichloronaphthalene with phosphorus pentachloride, tetrachloronaphthalene is obtained (m. p. 159·5—160·5°). When the dinitro-compound is reduced with acetic acid, hydrochloric acid and tin, it furnishes a diamidodichloronaphthalene,  $C_{10}H_4Cl_2(NH_2)_2$ , (m. p. 204—205°). When the same dinitro-derivative is acted on with alcoholic potash, the nitro-groups are left intact; but the chlorine is replaced by OEt. Thus a nitroethoxynaphthalene,  $C_{10}H_4(NO_2)_2(OEt)_2$ , is obtained, crystallising in small yellow needles (m. p. 228—229°).

J. I. W.

**Ethlynaphthalene and some of its Derivatives.** By C. MARCHETTI (*Gazzetta*, **11**, 439—442).—This hydrocarbon, obtained by acting on ethyl chloride and naphthalene with aluminium chloride, and submitting the product to fractional distillation, is easily purified by repeated crystallisation of its picric acid compound (m. p. 71°), which is more soluble in alcohol than that of naphthalene. Ethlynaphthalene is a limpid, colourless liquid (b. p. 251°), of sp. gr. 1·0078, referred to water at 0°. The sulphonic acid formed on heating the hydrocarbon with sulphuric acid at 80°, appears to contain two compounds, one in far larger proportion, yielding a solid ethlynaphthol on fusion with potash, the other a liquid; there is no evidence, however, to show that the latter is a naphthol. The acids were converted into lead salts, and separated by fractional crystallisation. *Ethlynaphthol*,  $C_{10}H_6Et.OH$ , prepared from the lead salt of ethlynaphthalene-sulphonic acid by fusion with potash in the usual way, crystallises from dilute alcohol in silvery white scales (m. p. 98°), almost insoluble in boiling water, but easily soluble in alcohol or ether. C. E. G.

**Ethereal Oil of Pinus Pumilio.** By A. ATTERBERG (*Ber.*, **14**, 2530—2532).—The oil extracted from the needles of *Pinus pumilio*, can be separated into four constituents by fractional distillation. The portion boiling above 200° is distilled in steam. The oil contains—

1. Terebenthene, b. p. 156—160°; rotatory power,  $-6\cdot66$ .
2. Sylvestrene, b. p. 171—176°; rotatory power,  $-5\cdot38$ .
3. A liquid which boils at 250° with decomposition, but is volatile in a current of steam. This terpene has the characteristic odour of the essential oil. Its rotatory power is  $-6\cdot2$ .
4. A viscous liquid, which cannot be distilled in steam. It is a polymerised terpene. W. C. W.

**Essence of Angelica.** By NAUDIN (*Compt. rend.*, **93**, 1146—1148).—The seeds of the angelica (*Archangelica officinalis*) of the family Umbelliferae, contains an essential oil of delicate odour. Sp. gr. at 0°, 0·872° rotatory power, with a thickness of 200 mm.  $[\alpha]_D = +26^\circ 15'$ . When fractionally distilled, the greater portion passes over at 174—184°; and on refractionation, the boiling point is found to be higher, owing to polymerisation. It readily absorbs oxygen from the air. When distilled under 22 mm. pressure, it boils constantly at 87°, forming a mobile colourless liquid, which boils at 175° under the ordinary pressure, and having the sp. gr. 0·833 at 0°, and an odour of

hops. It produces a suffocating sensation when inhaled, similar to that produced by the amyl-compounds. It is a terebenthene, its analyses agreeing with the formula  $C_{10}H_{16}$ ; when heated at  $100^{\circ}$  in a closed tube, it becomes viscid. Its rotatory power is the same as that of the essential oil, but it slowly decreases on heating at  $100^{\circ}$ , until it reaches a limit of  $9^{\circ} 44'$  after 432 hours.

	[ $\alpha$ ] <sub>D</sub> .	
Rotatory power.....	25°	16'
After heating at $100^{\circ}$ for 144 hours ..	19	0
"      "      288      "      ..	12	7
"      "      432      "      ..	9	44

The same result is obtained by heating at  $180^{\circ}$  for six hours, the hydrocarbon becoming pasty and of a pale-brown colour, owing to polymerisation. Like the  $\beta$ -isoterebenthene of Riban, this hydrocarbon (called by the author *terebangelene*) readily oxidises, which explains the presence of 30 per cent. of a resinous body in the essential oil. Chlorine and bromine act violently on terebangelene, forming cymene, and at  $100^{\circ}$  it is readily polymerised by sodium.

In the essential oil (two years old and containing moisture) the author observed a white crystalline body, containing oxygen, probably a hydrate of terebangelene, but the small quantity obtained prevented further study.

The root of the plant furnishes an essential oil of acrid taste and smell, which the author intends to study, with the view of establishing its identity with the oil from the seeds. L. T. O'S.

**Terpin.** By W. E. WALITZKY (*Compt. rend.*, **94**, 96—98).—The following results have been obtained in studying the properties of the alcohol with which cholesterin may be compared, on the supposition that it is an alcohol of the hydrocarbon  $(C_5H_8)_n$ , in which one or two atoms of hydrogen are replaced by other alcohol radicals.

When 10—12 grams of terpin are treated with 60 grams of a cold mixture of equal weights of sulphuric acid and water, no rise in temperature occurs, but a transparent liquid rises to the surface, which, after washing with soda and baryta-water, and distillation in a vacuum over sodium, boils at  $176.5$ — $181.5^{\circ}$ . It is without action on polarised light, of sp. gr. 0.93 at  $0^{\circ}$ , and its analysis and vapour-density correspond with the formula  $C_{10}H_{16}$ . It does not form crystalline compounds with hydrochloric acid or bromine.

This hydrocarbon, which the author proposes to call *terpinene*, is also obtained from the terpin by shaking with a warm mixture of 3 parts nitric acid and 5 parts water; also by the action of glacial phosphoric acid at  $50$ — $80^{\circ}$ , and glacial acetic acid at  $200^{\circ}$  under pressure. No ether results from the action of acetic acid or acetic chloride on terpin. Phosphorus pentachloride reacts energetically with terpin, forming the hydrochloride  $C_{10}H_{16}(HCl)_2$ , [which decomposes above  $110^{\circ}$ , with elimination of hydrochloric acid. This hydrochloride, heated in sealed tubes with water and silver oxide, yields a liquid containing no chlorine.

The terpin prepared according to the direction of St. Clare-Deville

and Berthelot is not formed more rapidly by agitation. The compound,  $C_{10}H_{16}(HO)_2 + H_2O$ , sublimes entirely between  $100^\circ$  and  $107^\circ$ , without fusion.

L. T. O'S.

**Helicin.** By H. SCHIFF (*Ber.*, 14, 2559—2562).—In support of the view that *helicin* contains an aldehydic OH group, the author points out that this glucoside forms crystalline compounds with acid sulphites. Tolylenediamine and benzidine combine with two molecules of *helicin*. A crystalline compound is also obtained by the action of urea on *helicin*, viz.,  $C_6H_{11}O_5 \cdot O \cdot C_6H_4 \cdot CH(NH \cdot CONH_2)_2$ .

W. C. W.

**Composition of Picrotoxin.** By L. BARTH and M. KRETSCHY (*Monatsh. Chem.*, 2, 796—809).—This paper is a reply to the criticisms of Paternò and Ogialoro (*Abstr.*, 1881, 440) on a former communication by the authors (*ibid.*, 286), in which they describe experiments leading to the conclusion that the substance commonly called picrotoxin (from *Cocculus indicus*) is a mixture of three definite compounds, viz., picrotoxin,  $C_{15}H_{16}O_6$ , bitter and very poisonous; picrotin,  $C_{25}H_{30}O_{12}$ , bitter, but not poisonous; and anamirtin,  $C_{19}H_{34}O_{10}$ , neither bitter nor poisonous. In the present paper, experiments are detailed confirming the composition and properties ascribed by the authors to picrotoxin and picrotin.

H. W.

**Chlorophyll.** By HOPPE-SEYLER (*Bied. Centr.*, 1881, 790).—The phosphorus compounds present in chlorophyllan can be removed by boiling with alcoholic potash; and this boiling also causes the formation of a new crystalline nitrogenous acid, chlorophyllanic acid, which is soluble in ether, and whose ethereal solutions possess the optical properties of chlorophyll. Besides this acid, glycerolphosphoric acid and cholin are produced from chlorophyllan. Chlorophyllan is not considered to be mixed with lecithin, but to form a compound with that substance, or at least a lecithin in which, like other lecithins, glycerol and cholin are in combination with phosphoric acid.

E. W. P.

**Contributions to the Knowledge of Chlorophyll.** By R. SACHSSE (*Bied. Centr.*, 1881, 790).—Oxidation of phyllocyanin with potassium permanganate in alkaline solutions yields palmitic, oxalic, and another acid. Nitric acid produces the same results. The new acid ( $C_5H_6O_4$ ) is uncrystallisable, and prevents the precipitation of iron and copper from their solutions by alkalis. Dry distillation of phyllocyanin produces the aldehyde of palmitic acid, and distillation with lime gives palmitone.

E. W. P.

**Quinoline.** By C. BEDALL and O. FISCHER (*Ber.*, 14, 2570—2575).—*Methoxyquinoline* is prepared by heating molecular proportions of hydroxyquinoline, methyl iodide, and potash dissolved in methyl alcohol in a flask provided with a reflux condenser. When the smell of methyl iodide disappears, the methyl alcohol is distilled off, and the residue is mixed with soda-lye and extracted with ether. On evaporating the

etheral solution, methoxyquinoline remains as a thick oily liquid, which is purified by redistillation.

The *hydrochloride*,  $C_{10}H_9NO \cdot HCl$ , crystallises in prisms, which are very hygroscopic, and dissolve readily in water and in alcohol. The *picrate*,  $C_{10}H_9NO + C_6H_3N_3O_7$ , is deposited from a hot alcoholic solution in yellow needles or plates, which are sparingly soluble in alcohol and water. The *platinochloride*,  $(C_{10}H_9NO \cdot HCl)_2PtCl_4$ , forms yellow needles, sparingly soluble in water and ether. By the action of tin and hydrochloric acid on methoxyquinoline, a tetrahydride is obtained, which unites with acids, forming crystalline salts. The *hydrochloride*,  $C_{10}H_{13}NO \cdot HCl$ , is deposited from a mixture of alcohol and ether in colourless prisms. The *platinochloride* crystallises in needles, which are soluble in alcohol and in hot water. The picrate is sparingly soluble in water. Methoxyquinoline tetrahydride gives an intense red coloration with ferric chloride. It also yields a crystalline nitroso-compound, which is deposited when sodium nitrite is added to a solution of the hydride in cold sulphuric acid. After recrystallisation from light petroleum, the *nitroso*-compound is obtained in flat prisms (m. p.  $80^\circ$ ), of a pale-yellow colour. It is soluble in benzene, chloroform, ether, and alcohol. It dissolves in strong hydrochloric or sulphuric acid, forming a carmine-red solution.

*Amidoquinoline*, prepared by the action of zinc ammonium chloride on hydroxyquinoline at  $180^\circ$ , is identical with the amidoquinoline obtained by W. Koenigs (*Ber.*, 12, 448) from quinoline.

*Quinoline cyanide* is prepared by heating 7 parts of dried sodium quinolinesulphonate with 2 parts of potassium cyanide. The distillate is washed with water to remove ammonium cyanide and carbonate, and then redistilled. Quinoline cyanide melts at  $87^\circ$ , and boils at  $360^\circ$ . It dissolves freely in alcohol, benzene, and carbon bisulphide, but is only sparingly soluble in water and in light petroleum.

On saponification with hydrochloric acid at  $140^\circ$ , quinoline cyanide yields quinolinebenzcarboxylic acid, which is identical with the acid obtained from meta-nitrobenzoic acid by Skraup and Schlosser (*Monatsheft*, 2, 518). This shows that the sulphonic group in quinolinesulphonic acid occupies the same position as the carboxyl group in quinolinebenzcarboxylic acid.

W. C. W.

**Complex Character of Morphine. Transformation into Picric Acid, and its Solubility.** By P. CHASTAING (*Compt. rend.*, 94, 44—4).—Reference is made to the phenolic character of morphine (*Abstr.*, 1881, 921) and to the acid obtained by the action of nitric acid (this vol., 73). This acid,  $C_{10}H_9NO_9$ , when heated with 1 mol. of water at  $100^\circ$ , under pressure, yields trinitrophenol.

*Solubility of Morphine.*—One litre of water at  $0^\circ$  dissolves only traces of the base; at  $10^\circ$ , 0.10 gram, and up to  $40^\circ$  the solubility increases directly with the temperature; from  $45^\circ$  to  $100^\circ$  the solubility increases more rapidly than the temperature, and the curve of solubility assumes a parabolic shape. The amount of morphine dissolved by 1 litre of water is found from the equation  $y^2 = 2px$ , where  $y$  is the temperature,  $x$  the solubility, and  $2p = 47$  from  $45$ — $55^\circ$ , and 46 from  $46$ — $100^\circ$ . If  $y = 100$ , then  $x = 2.17$  grams.

L. T. O'S.



**Compound of Quinine and Quinidine.** By C. H. WOOD and E. L. BARRET (*Chem. News*, **45**, 6—7).—An ethereal solution of the total alkaloids from cuprea bark frequently deposits crystals which are different from those of any of the known cinchona alkaloids obtained under like circumstances. These crystals consist of a compound of quinine and quinidine (probably in equal proportions), as is proved by the fact that they are likewise produced when the pure alkaloids are dissolved together in ether and allowed to crystallise. They are much less soluble in ether than either of the constituents, 100 c.c. of ether at the ordinary temperature only dissolving 0.5 gram of the compound. T. C.

**Distillation of Cinchonine with Potash.** By O. DE CONINCK (*Compt. rend.*, **94**, 87—90).—The base parvoline, which the author announced as being formed among others by the action of potash on cinchonine (Abstr., 1881, 56 and 443), has by repeated fractionation been separated into three bases.

Fraction I, 210—215°, consisting of *tetrahydroquinoline*,  $C_9H_{11}N$ , sp. gr. 1.06 at 0°, is a mobile oily liquid, scarcely colouring when exposed to sunlight, slightly hygroscopic, and insoluble in water, but very soluble in acids. Its hydrochloride,  $C_9H_{11}N.HCl$ , crystallises in fine deliquescent needles, very soluble in water. By adding platinum chloride to the hot concentrated aqueous solution and evaporating in a vacuum, pale orange-yellow plates are deposited of the composition  $(C_9H_{11}N.HCl)_2.PtCl_2$ . The facility with which this compound is formed distinguishes this base from the other pyridine bases, the platinochlorides of which it is necessary to boil for some time, in order to convert them into compounds similar to the above. The platinochloride and platinichloride of this base melt before decomposing, thus differing from those of quinoline, which swell up and char without melting. The platinochloride  $(C_9H_{11}N.HCl)_2.PtCl_4$  is obtained as a yellow-orange, crystalline precipitate, by adding a dilute solution of platinum chloride to a cold concentrated solution of the hydrochloride, or in long needles, by allowing a mixture of the dilute solutions to stand. The base obtained from the platinochloride boils at 212—213°; it reduces ferric chloride, a property possessed also by the synthetic tetrahydroquinoline. This base, however, boils at 244°.

Fraction II, 220—226°, obtained only in small quantities, yields a yellow crystalline platinochloride, of the composition—



it is therefore either dihydroquinoline, a product of the decomposition of the preceding base, or perhaps a mixture of the latter with quinoline, but the small quantity obtained prevented further examination.

Fraction III, 226—231°, is of strong disagreeable odour, and when treated with platinum chloride yields an amorphous yellow powder, of the constitution  $(C_9H_7NHCl)_2.PtCl_4$ . The greater portion of the fraction distils between 228—230°, and the analyses show that it is probably quinoline, or an isomeride mixed with a small quantity of the preceding base. Since Baeyer and Skraup have synthetically obtained two isomeric quinolines (b. p. 228°, and 232—233°), it is very

probable that the isomerides exist together in the crude base. The tetrahydroquinoline is intermediate between the quinoline and pyridine series.  
L. T. O'S.

**History of Tropine.** By K. KRAUT (*Ber.*, **14**, 2674—2676).—A controversial paper containing no new facts.

**Synthesis of Nitrogenised Colloïds.** By E. GRIMAUZ (*Compt. rend.*, **93**, 771—773).—The author, following the results of Schützenberger's researches, proposes to define proteïd substances as nitrogenised colloïds, which by hydration split up into amidated acids, carbonic acid, and ammonia. When aspartic anhydride is heated for two hours at 125—130° with half its weight of urea, it is changed into a thick mass, entirely soluble in boiling water. The solution is gummy, filters with difficulty, and has all the characters of a colloid substance; it is precipitated by acids, by alkaline salts, by magnesium and aluminium sulphates, by salts of iron, copper, and mercury, and by tannin; these precipitates are all gelatinous, and are so thick that, unless the solutions are very dilute, the vessels containing them may be inverted without loss. The jelly yielded by acetic acid is transformed by desiccation into translucent plates, having the appearance of dried albuminoïd substances; it is then insoluble in boiling water, which only softens it. It dissolves in potash, and the alkaline solution treated with copper sulphate becomes of a violet colour, giving exactly the same tint as proteïd substances. Aspartic anhydride by itself also gives this reaction.  
R. R.

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## Physiological Chemistry.

**Feeding Horses with Maize.** By A. MÜNTZ and others (*Bied. Centr.*, 1881, 766—769).—A series of reports from individuals companies employing large numbers of horses, from which it is gathered that the replacement of oats to a great extent by maize is accompanied by very satisfactory results. E. W. P.

**Comparison of the Digestibility of Peas by Horses and Sheep.** By E. WOLFF and others (*Bied. Centr.*, 1881, 760).—The following is a table of the digestive coefficients, being the mean results obtained with one horse and two sheep fed on meadow hay and peas :—

		Dry matter.	Organic matter.	Albumi- noids.	Fat.	Fibre.	Non-nitro- genous extract.
Hay	{ Horse ....	47·1	48·1	59·7	24·8	35·4	56·0
	{ Sheep ....	54·8	57·3	56·3	55·5	51·0	62·1
Peas	{ Horse ....	77·2	80·3	83·0	6·9	8·0	89·0
	{ Sheep ....	88·3	89·6	88·9	74·7	65·6	93·3

If, however, allowance is made for the nitrogen present in forms other than albuminoid, then the digestive coefficients for the proteïds are reduced to 55.6 (horse) and 51.6 (sheep). E. W. P.

**Loss of Substance Experienced by Starving Graminivora.** By M. RUBNER (*Bied. Centr.*, 1881, 753—760).—The animals experimented on were rabbits, and the amount of nitrogen excreted by them when starving, was determined only when 22 hours had elapsed since the last feeding; moreover, only the nitrogen in the urine was estimated, as the quantity in the fæces was considered to be too insignificant. The whole amount of nitrogen in the animal being known by analysis after death, the percentage of the nitrogen lost by excretion on the original quantity of nitrogen is calculated, and this shows that after the first few days of fasting, the excretion diminishes, but greatly increases during the few days previous to death; during the first period 2—3 per cent. of the albuminoids present pass away, but at the end 8 per cent. Compared with Carnivora, Graminivora of like weight lose as much nitrogen.

As regards loss of fat, this decreases as time passes, so that finally hardly any carbon appears in the urine, and that passing away by respiration is greatly diminished. It is unnecessary to reproduce the calculations employed, but it is shown that for every 43.3 grams fat, 100 grams nitrogenous matter are destroyed, and that from this latter quantity 41.5 parts fat can be formed, and it is in this ratio that fat and albumin are equivalent to one another. E. W. P.

**Excretion of Uric Acid by Birds.** By P. CAZENEUVE (*Compt. rend.*, 93, 1155—1157).—The results of the author's experiments show that the proportion between the amounts of uric acid, urea, and ammonia, excreted by birds, is not influenced by an increase or decrease of oxidation, but that the total amount excreted varies with the quantity of the nourishment taken, which quantity is connected with the stimulating or depressing effects of the medium.

It may be concluded therefore that the albuminoid matters in the system undergo a decomposition depending on hydration rather than oxidation.

The birds used in the experiments were sparrow-hawks, which were fed on the liver and lungs of calves. L. T. O'S.

**Distribution of Arsenic in the Animal Organism after Administration of Arsenious Anhydride.** By E. LUDWIG (*Chem. Centr.*, 1881, 90—95; 110—112; and 121—128).—From experiments on eight dogs, the author concludes, contrary to Scolosuboff, that in all cases, whether of acute or chronic poisoning, the liver is the organ richest in arsenic. When estimated quantitatively, the liver contained, weight for weight, approximately 17 times the amount of arsenic in the brain.

In the organs of men poisoned by arsenic, the author found the same general results. In a typical case of acute poisoning, the brain contained, per 100 grams, 0.00004 gram; the liver per 100 grams, 0.00338 gram of arsenic.

The author considers that the liver is by far the best organ to examine for arsenic in judicial cases, as it is always richer in it than other organs, and in cases of chronic poisoning still retains sufficient arsenic for identification 40 days after the last administration. F. L. T.

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## Chemistry of Vegetable Physiology and Agriculture.

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### Influence of Acids on the Formation and Activity of Yeast.

By M. HAYDUCK (*Bied. Centr.*, 1881, 782).—The results of the research will be best shown by the following table:—

Fermentation is aided by—

Sulphuric acid .....	0.02 per cent.
Lactic „ .....	0.2—0.1 „

Fermentation is retarded by—

Sulphuric acid .....	0.2 per cent.
Hydrochloric acid ....	0.1 „
Phosphoric „ ....	0.4—0.5 „
Lactic „ ....	2.5 „

Fermentation is suppressed by—

Sulphuric acid .....	0.7 per cent.
Hydrochloric acid .....	0.5 „
Phosphoric „ .....	1.3 „
Lactic „ .....	4.6 „

Formation of yeast is aided by—

Sulphuric acid .....	0.02 per cent.
Lactic „ .....	0.1—0.05 „

Formation of yeast is retarded by—

Sulphuric acid .....	0.07 per cent.
Lactic „ .....	1.5 „

Formation of yeast is suppressed by—

Sulphuric acid .....	0.2 per cent.
Lactic „ .....	4.0 „

E. W. P.

**Effect of Gases on the Splenic Fever Bacilla.** By T. SZPILMANN (*Bied. Centr.*, 1881, 789).—These bacillæ do not increase in carbonic anhydride, and they lose their activity only when the whole of the oxygen is replaced by carbonic anhydride. The corpuscles in blood affected by splenic fever are destroyed by ozone, but not so the bacillæ, which retain all their properties.

E. W. P.

**Sprouting Barley.** By G. DAY (*Bied. Centr.*, 1881, 789).—Barley when sprouting absorbs more oxygen than is required for the carbonic anhydride produced, and the quantity absorbed is in no definite ratio to the gas given out. Carbonic anhydride and water are eliminated in the proportion of 1 mol.  $\text{CO}_2$  to 1 mol.  $\text{H}_2\text{O}$ . E. W. P.

**Development of Oats.** By P. P. DÉHÉRAIN and MEYER (*Ann. Agronomiques*, 7, 197—217).—*Fourth Year of Observation.*—The observations made in 1879 were especially directed towards the solution of the questions:—(1) Is the loss of dry matter sometimes observed during the last days of vegetation an accidental or a regular phenomenon? (2) Was the small percentage of albuminoids in the 1878 crop (*Ann. Agronomiques*, 5, 145) due to exhaustion of the soil by carrying four successive crops of oats without manure, or should it be attributed to the influence of the season?

The authors show that the apparent loss of dry matter is due to irregular ripening, the oats which ripen earliest falling off and being lost, and that there is, on the contrary, really a gain of dry matter during the actual ripening. As regards the second question, the poverty of the 1878 seed in nitrogen was due to a *temporary* exhaustion of the nitrates in the soil by the excessive rain of 1878, the 1879 harvest not showing any deficiency. The 1878 harvest, although poor in nitrogen, rather exceeded that of 1879 in total dry weight; the formation of carbohydrates therefore proceeded without check, although the plant could not elaborate its normal proportion of albuminoids.

*Fifth Year of Observation.*—In the year 1880 the experimental crop of oats continued to increase in total dry weight during the ripening of the grain; thus confirming the observations of 1879, and showing that the losses observed in 1876 and 1878 were accidental, and due to the character of the seasons. In 1876 and 1878, in which the harvest was early, there was a notable loss in dry weight, but the crop was nevertheless heavier than in the years 1877, 1879, and 1880, years of late harvests, during which there was no loss of dry matter.

The quantity of ash contained in annual plants increases with their age: the oat-straw contained less ash in 1879 and 1880 than in 1878, and the ash contained less silica; this deficiency of silica is probably to be attributed not to the exhaustion of soluble silica in the soil, but to the fact that, 1879 and 1880 being late seasons, the plants had scarcely finished their development when harvested.

J. M. H. M.

**Effect of Light on Transpiration in Plants.** By O. COMES (*Bied. Centr.*, 1881, 789).—The transpiration of water is affected by light as well as by the other physical agencies influencing evaporation of water, therefore plants transpire more in daylight than in the dark, and the amount is proportional to the intensity of the light, the maximum taking place shortly after midday, and those parts of the plant transpire most which are the most intensely coloured, and only those light rays produce transpiration which are absorbed.

E. W. P.

**Influence of Light on the Respiration of Seeds during Germination.** By PAUCHON (*Bied. Centr.*, 1881, 789).—The amount of carbonic anhydride exhaled by a castor-oil plant growing in the dark was greater than that from one in the light. For a bean plant in the dark, the ratio  $\text{CO}_2 : \text{O}$  was one-third less than that for the castor-oil plant, but as time proceeded the ratio approached closer to unity. Comparing the ratios obtained with the same plant in darkness and light, the ratio  $\text{CO}_2 : \text{O}$  in the dark exceeds that in the light by a quarter, and the absolute amount of carbonic anhydride exhaled is less in the light than in the dark. The results obtained are considered by the author sufficient to account for the formation of asparagine.

E. W. P.

**Ripening of certain Annuals.** By P. P. DÉHÉRAIN and E. BREAL (*Ann. Agronomiques*, 7, 161—197).—The experiments described in this paper were undertaken by the authors with a view to decide the question as to whether or not a loss in total dry matter is a general phenomenon accompanying the ripening of annual plants. The general conclusions to which their researches have led are summed up as follows:—

1. The alteration in dry weight which annuals undergo during ripening, enables us to classify them in three groups.—

- (a.) Plants which diminish in weight soon after flowering, and which gradually wither and die (*Collinsia bicolor*, *Sinapis nigra*).
- (b.) Plants which diminish in dry weight during the ripening of the seed, but retain sufficient vigour to cause a renewal of growth afterwards (*Eschscholtzia californica*, *Delphinium Ajacis*, *Convolvulus tricolor*, *Clarkia elegans*).
- (c.) Plants which continue to augment in weight during the ripening of the seed (*Sinapis alba*, *Silene pendula*, *Hesperis maritima*, *Papaver somniferum*).

2. The diminished vitality which always accompanies the ripening, even when no loss in dry weight occurs, appears to be due to transport of the nitrogenous matter from the leaves to the seeds, determining the withering or death of some of the leaves.

3. The diminution of the total mineral matter may be explained by the falling off of some of the leaves, or by their destruction by slow oxidation, accompanied by dispersion of the contained minerals.

4. None of the observed facts favour the hypothesis of a return of the mineral matters to the soil by excretion through the roots.

J. M. H. M.

**Influence of Light on the Ripening of Grapes.** By A. LÉVY (*Ann. Agronomiques*, 7, 230—238).—The observations made on this subject by the author in 1879 have already appeared (*Abstr.*, 1881, 930). In 1880, the author repeated these observations on a larger scale, and with certain improvements in the apparatus, which had the effect of rendering the conditions of temperature still more nearly identical in the case of the clusters exposed to, and sheltered from, the light. The results of the 74 analyses made in 1880 entirely confirm



those already published. The mean percentage of sugar in the grapes exposed to light (37 analyses) is 19·72, and of acids 5·67; in the grapes ripened in darkness (37 analyses), sugar 16·13, acids 6·90. The grapes ripened in sunlight thus contain 3·59 per cent. more sugar and 1·237 less acids than those ripened in darkness.

J. M. H. M.

**Chemical Studies on the Vegetable Skeleton.** By E. FRÉMY and URBAIN (*Compt. rend.*, 93, 926—931).—This paper, which is a continuation of the numerous investigations of Frémy on this subject, gives the relative proportions of the various substances, viz., pectose and its derivatives, cellulose, paracellulose, metacellulose, vasculose, and cutose, which are contained in the skeleton of different plants. The methods of estimation depend on the following properties of these bodies:—*Pectose* is dissolved by alkaline carbonates, and is reprecipitated as a gelatinous insoluble precipitate on the addition of hydrochloric acid. *Cellulose* and its two isomerides dissolve without coloration in concentrated sulphuric acid, but the three compounds differ from one another, in that cellulose dissolves immediately in an ammoniacal solution of cupric oxide; paracellulose dissolves therein only after treatment with acids, whilst metacellulose is insoluble in this reagent, but is easily soluble in nitric acid or in hypochlorites. *Vasculose*, the chief constituent of the vessels which bind together the fibres and cells, is also insoluble in ammoniacal copper solution after treatment with acids, and withstands for a long time the action of concentrated sulphuric acid, but is quickly attacked by such oxidising agents as chlorine, hypochlorites, nitric acid, chromic acid, and permanganate, and is thereby converted into resinous substances which are soluble in alkalis; it is also dissolved when heated with caustic alkalis under pressure, on which depends the preparation of wood and straw for the manufacture of paper. Finally, *cutose*, which forms the transparent membrane which protects those organs of plants exposed to the air, differs from vasculose, which it greatly resembles in other respects, in the fact that it dissolves in dilute caustic alkalis even under ordinary pressure. All parts of plants, the wood, leaves, buds, fruits, &c., were investigated. The wood of the trunks of various trees contained as follows:—

	Vasculose.	Cellulose and paracellulose.
Poplar .....	18	64
Oak .....	28	53
Box .....	34	28
Ebony .....	35	20
Rock-wood .....	36	21
Iron-wood .....	40	27

The amount of vasculose increases, therefore, with the hardness and density of the wood. The parenchyma of elder-pith contains 37 per cent. cellulose, 38 per cent. paracellulose, and 25 per cent. vasculose; in cork-wood there is 5 per cent. of bodies soluble in acids and alkalis, 12 per cent. cellulose and paracellulose, 43 per cent. cutose, and 29 per cent. vasculose. Ivy leaves contain 707·7 parts of water and

bodies soluble in neutral solutions, 240 parts of parenchyma consisting of cellulose and pectose, 17·3 parts of vessels and fibres consisting of vasculose and paracellulose, and 35 parts of epidermis consisting of cutose and paracellulose. The petals of the dahlia contain 961·3 parts of water and soluble matter, 31·63 parts of parenchyma (cellulose and pectose), 1·2 part vasculose, 2·27 parts paracellulose, 3·6 parts cutose. The epicarp of most fruits, as of apples and pears, consists of three membranes, of which the outermost consists of cutose, the middle of vasculose, and the innermost of paracellulose; the endocarp is similar in composition to the wood, and is the harder the more vasculose it contains. Thus in the shells of various nuts were found:—

	Vasculose.	Cellulose and paracellulose.
Walnut.....	44	25
Hazelnut .....	50	31
Cocoa-nut.....	58	25
Apricot kernel.....	60	26
Bankoul-nut .....	62	14

The mesocarp of fruits consists chiefly of cellulose, frequently accompanied by pectose, the vessels of the mesocarp chiefly of vasculose, and the stony concretions of the mesocarp in pears of a mixture of vasculose and cellulose. The perisperm of the seed, after removal of the starch, fat, and nitrogenous substances, consists almost entirely of cellulose, and the testa of a mixture of cutose, cellulose, and paracellulose. The tissues of fungi contain considerable quantities of metacellulose.

T. C.

**Presence of Free Fatty Acids in Vegetable Fats.** (*Dingl. polyt. J.*, 242, 454.)—Hofmann found traces of free fatty acids in human fat, and Rechenberg obtained similar results with beef and pork fat.

No direct determinations of fatty acids in vegetable fats have been made. König and Becke, however, conclude from glycerol determinations that vegetable fats consist essentially of free fatty acids.

Rechenberg has investigated various seed-oils as to the percentage of free fatty acids. The following table gives the milligrams of potassium hydroxide necessary to neutralise 100 grams of the fats:—

Seed.	This year's.			Last year's.	5 to 6 years'.	Over 10 years'.
	1.	2.	3.			
Common white turnip ( <i>Brassica rapa</i> )	133	74	36	87	205	—
Winter rape ( <i>B. napus</i> ) .....	2137	138	32	87	542	—
Gold of Pleasure ( <i>Camelina sativa</i> ) ..	2070	—	324	313	676	—
Linseed ( <i>Linum usitatissimum</i> ) .....	—	445	53	167	425	—
Radish ( <i>Raphanus sativus</i> ) .....	—	—	142	—	—	2580
Poppy ( <i>Papaver somniferum</i> ), blue ..	—	—	743	557	—	2060
" " " white..	—	—	913	—	—	—

1 and 2 are unripe seeds, 3 partly ripened seeds.

D. B.

**Composition of Duck-weed (*Lemna triscula*).** By A. MAYER (*Bied. Centr.*, 1881, 786).—This plant, which grows in stagnant water, is recommended as a material for composts: it contains—

	Air-dry.	Wet.
Water.....	8.5	94.3 per cent.
Albuminoids.....	23.8	1.8 "
Fat.....	3.9	0.2 "
Fibre.....	9.0	0.6 "
Soluble carbohydrate	32.2	2.0 "
Ash.....	18.1 { (containing ) 2.2 P <sub>2</sub> O <sub>5</sub> }	1.1 "

E. W. P.

**Chemical Nature of the Cytoblast.** By E. ZACHARIAS (*Bied. Centr.*, 1881, 790).—The cytoblast or cell-nucleus consists principally of nucleïn. It is distinguished from other albuminoids, not only by its composition, but also by distinct chemical reactions.

E. W. P.

**Physico-chemical Changes produced in Potato-starch by Boiling.** By T. MAGERSTEIN (*Bied. Centr.*, 1881, 791).—The hydration of the starch grains may vary, the difference being due to boiling or steaming, or steaming under pressure. For normal hydration, 1 part starch to 5.5 water, is sufficient. The space occupied by the hydrated starch is less rather than greater in proportion to the space occupied by the starch, together with the hydrating water.

E. W. P.

**New Instances of Phosphorescence in Plants.** By L. CRIÉ (*Compt. rend.*, 93, 853).—Phosphorescent light has been recently noticed by the author to be emitted by the following plants:—*Tropeolum majus*, *Agaricus olearius*, *Auricularia phosphorea*, *Polyporus citrinus*. The *rhizomorphs*, or vegetative apparatus of many mushrooms, are also phosphorescent, and are common in mines. He also mentions *Rhizomorpha setiformis* and a peculiar kind of *rhizomorpha*, which he has found within branches of elder, where they are developed between the wood and the pith. *Xylaria polymorpha* was also found emitting a faint white light, a circumstance not before noted in a plant of this kind. The phosphorescence of *Rhizomorpha* and *Xylaria* is attributed by the author to the respiration of the conidiophores.

R. R.

**Contributions from the Experimental Station at Halle on Fodder.** By M. MÄRCKER (*Bied. Centr.*, 1881, 762–766).—New analyses of various fodders show that caution must be exercised when employing the mean analytical composition of grains, &c., as so many circumstances tend greatly to alter their composition, and that the published means can be safely made use of only when the crop is in good condition and has been well nourished. Analyses of hay are given, showing the influence of weather and manuring on its composition.

E. W. P.

**Cultivation of Cock's-foot Grass (*Dactylis Glomerata*), in Saxony.** By F. NOBBE (*Bied. Centr.*, 1881, 771–773).—Examination

of various samples of the above grass, purchased for sowing in Saxony, showed great variations in the weight of the seeds, in their germinating power, and in the purity of the sample, there being always a mixture of other seeds, sand, &c. The author considers that it would be greatly advantageous to the cultivator if more care were taken in the preparation of the samples of grass seeds for cultivation. The same remarks apply to the samples of *Poa pratensis*. E. W. P.

**On Fodder Cabbages.** By H. LEIZOUR and NIVET (*Ann. Agronomiques*, 7, 307—316).—Experiments were undertaken by the authors to determine the relative yield and nutritive value of the different varieties of cabbage cultivated as fodder crops in Brittany. The principal results are embodied in the annexed table:—

Variety.	Remarks.	Yield per hectare.	Observations.
		Kilos.	
1. Spreading Poitou (Vilmorin's seed)	Very much branched	26,704	27·45 p. c. frozen.
2. Thousand-headed .....	More branched than the preceding	26,074	15·29 „
3. Flanders or Red Cavalier	Resisted cold well ..	22,037	1·17 „
4. Spreading Poitou (seed grown at the school)	—	18,626	23·56 „
5. Cavalier or Cow Cabbage	Good cropper; not much affected by cold	17,724	2·74 „
6. Red ( <i>Moellier rouge</i> ) ..	—	17,131	34·47 „
7. White ( <i>Moellier blanc</i> )	Succulent; not hardy	14,420	39·21 „

The first cutting of leaves was made September 24th, and the second November 20th. The yield per hectare includes the stamps. The minimum temperature was  $-9^{\circ}$  C., on January 21st and 22nd. Analyses of the stems and leaves of all the above crops are given in the authors' paper. In the following table they are classified according to the total albuminoids ( $N \times 6.25$ ) yielded per hectare by the stems and leaves together:—

Variety.	Albuminoids per cent. of dry matter.		Total albuminoids per hectare. Kilos.
	Leaves.	Stems.	
1. Thousand-headed .....	28·24	11·47	911,274
2. Poitou (Vilmorin) .....	24·80	13·57	815,546
3. „ (Lezardeau) .....	23·34	11·97	702,939
4. Flanders .....	12·26	13·23	659,189
5. Cavalier .....	20·60	13·55	608,128
6. <i>Moellier blanc</i> .....	21·80	15·44	525,306
7. <i>Moellier rouge</i> .....	27·30	13·69	501,951

The authors' analyses show that the cabbage is richer in nitrogenous substances than has hitherto been supposed, and that its nutritive value and "albuminoïd ratio" are therefore greater than those generally given.

J. M. H. M.

**Value of Different Varieties of Sugar-beet.** By M. MÄRCKER (*Bied. Centr.*, 1881, 773).—Tables of the amount of sugar, &c., produced by different kinds of sugar-beet.

E. W. P.

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## Analytical Chemistry.

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**Use of Palladium for Absorbing the Hydrogen set free in Sealed Tubes during certain Reactions.** By A. TCHIRIKOFF (*Journ. Russ. Chem. Soc.*, 1881, 47—48).—On placing palladium wire in a sealed tube, in the lower part of which zinc was acted on by hydrochloric acid, all hydrogen was absorbed. Again on heating the alloy  $\text{Pd}_2\text{H}$ , all the hydrogen was set free. The author recommends this as a process for the preparation and storage of perfectly pure hydrogen for eudiometric purposes. B. B.

**On the Constancy of Thiosulphate Solutions.** By S. U. PICKERING (*Chem. News*, 44, 277—279).—The strength of the solutions was found thus:—A given volume of a standard potassium dichromate solution was treated with definite quantities of potassium iodide and hydrochloric acid. A certain volume of the thiosulphate solution, sufficient to be very nearly equivalent to the liberated iodine, was then added, and the small quantity of iodine which still remained free was determined by a standard solution of thiosulphate, the strength of which had been previously ascertained. Corrections for acid added and temperature were made as previously directed (*Chem. Soc. J.*, 1880, 128). It is shown that it will keep perfectly, provided no organic matter be present in the water used for making the dichromate solution. All the solutions were approximately decinormal. Two series of experiments were made on sodium thiosulphate. The following are the end results, the strength of the freshly prepared solution being calculated to 100.0, and the others in proportion:—

	Strength after 365 days.	
	I.	II.
Solution in white bottle in diffused daylight	98.60	97.50
„ blue „ „	98.75	98.14
„ „ „ the dark .....	98.94	99.86
	(after 5 days)	
„ „ „ diffused daylight, a trace of potash added .....	98.84	—
Solution in blue bottle in diffused daylight, 5 grams ammonium carbonate per litre added .....	95.95	—
Solution in blue bottle in strong daylight and sunlight, after 421 days.....	—	92.37

The difference in the first two (No. II) is due to the bottles being nearly empty at the finish of the experiments, and the consequent action of the air. This action is shown by experiments on a solution of potassium thiosulphate; after 365 days, its strength had decreased to 98.75, *i.e.*, 1.25 per cent., but during another three months, the bottle being now nearly empty, it decreased to 96.0, *i.e.*, a loss of 2.75 per cent. Two other samples of potassium thiosulphate solution, the one in a blue, the other in a white glass bottle, exposed to diffused daylight, had, after 365 days, the strengths 98.16 and 98.04. In conclusion, the solution should be kept in a bottle of blue glass, or preferably in the dark, and should be protected as much as possible from the air. A very small quantity of potash may be added with advantage, in accordance with the experience of A. V. Harcourt, but the addition of ammonium carbonate, as recommended by Rose, is decidedly injurious.

H. B.

**Estimation of "Plaster" in Wines.** By E. HOUDARD (*Bull. Soc. Chim.* [2], 36, 546—547).—The apparatus required consists of ten test-tubes, in two rows of five each, a 25 c.c. pipette, graduated in 5 c.c., and a burette, graduated in five divisions in such a way that each division is 0.5 c.c. larger than the preceding one. 5 c.c. of the wine to be tested are run from the pipette into each of the first row of test-tubes, and Marty's standard solution (10 c.c. = 0.1 gram potassium sulphate) is then added in such a way that a quantity corresponding to the first division (0.5 c.c.) is added to the first tube, a quantity corresponding to the second division (1.0 c.c.) to the second tube, and so on. Boil, filter the contents of each tube into the corresponding tube of the second row, and then add a drop of the standard solution to each tube, and observe in which a slight turbidity is produced. If a turbidity is produced, for example, in tube No. 2, but not in No. 3, then the wine contains more than 2 grams potassium sulphate per litre, but less than 3 grams. With practice the amount of sulphate may be rapidly estimated to within 0.25 gram per litre.

C. H. B.

**Electrolytic Estimations and Separations.** (*Dingl. polyt. J.*, 242, 440—444.)

*Cobalt.*—On treating a solution of a salt of cobalt with an excess of potassium oxalate, and subjecting the clear solution to electrolysis, the red coloration is rendered dark-green, which colour diminishes in intensity as cobalt is separated metallically on the negative electrode. A better and quicker separation of the metal is effected by replacing the potassium oxalate by the ammonium salt. By exposing the hot solution to the electric current, cobalt is obtained in the form of a firmly adhesive coating of a grey colour.

*Nickel.*—The determination of nickel may be conducted in a similar manner, the metal adhering firmly to the electrode in the form of a grey coating.

*Iron.*—This metal separates as a shining, steel-grey, firmly adhesive mass. The reduced iron may be exposed to the air for days, without showing signs of oxidation.

*Zinc* separates with a dark-grey colour, the metal being soluble in dilute acids with difficulty.

*Manganese* is completely precipitated by converting it into the soluble double compound (by the addition of an excess of potassium oxalate), and passing an electric current.

*Bismuth* does not adhere to the electrode as firmly as the above-mentioned metals: hence it is necessary to use a very large surface for the deposition, in order to avoid any loss of metal on subsequently washing the mass with water, alcohol, and ether.

*Lead*.—The electrolytic determination of this metal cannot be recommended, owing to the rapid oxidation of the deposited metal.

*Copper* separates from the double salt of ammonium oxalate very readily. An excess of oxalate should be present, and a strong current used.

*Cadmium* and *ammonium* oxalates when subjected to electrolysis, precipitate cadmium as a grey coating, which adheres sufficiently to the electrode to allow of its being washed without loss.

*Tin* separates from its hydrochloric acid solution as readily as from the double salt of ammonium oxalate, in the form of a fine silver-grey layer.

*Antimony* separates from its hydrochloric acid solution in the metallic state, but does not adhere firmly to the electrode. The reduction is facilitated and the separation effected more completely by treating the solution with sulphuretted hydrogen, neutralising with ammonia, and adding ammonium sulphide. The precipitate produced has a light grey colour, and adheres firmly to the electrode.

*Arsenic* cannot be separated quantitatively by electrolysis.

For the separation of iron and manganese, the solution of iron, manganese, and ammonium oxalate is subjected to electrolysis. However, the separation of both metals is successful only when the formation of manganese dioxide is prevented until the greater part of the iron has been deposited, which is accomplished either by the addition of sodium phosphate, or by using a large excess of ammonium oxalate.

*Quantitative Separation of Iron and Aluminium*.—By subjecting the solution of iron-ammonium and aluminium-ammonium oxalate, treated with excess of ammonium oxalate, to electrolysis, iron first separates on the negative electrode, in the form of a firmly-adhering layer, whilst aluminium oxide remains in solution so long as the quantity of ammonium oxalate is greater than the quantity of ammonium carbonate produced.

D. B.

**Investigation of Iron and Iron Ores.** (*Dingl. polyt. J.*, 242, 435—439.)—For the determination of ferric oxide in iron ores, Pszczolka recommends the titration method with sodium thiosulphate and potassium iodide, the process which he adopts being described more minutely in the original paper.

Referring to the potassium permanganate method, Sorge mentions that it is not absolutely necessary to dissolve the iron ores in sulphuric acid, which frequently gives rise to imperfect solution, but that accurate results are obtained in the presence of a small quantity of free hydrochloric acid, provided that largely diluted and cold solutions are



operated on. Sorge recommends titrating the ferric oxide with stannous chloride and iodine, the method which he proposes to adopt being rapid in execution, and enabling the worker to use a concentrated hydrochloric acid solution of the iron-ore.

For the determination of silicon in pig-iron and steel, Brown and Shimer dissolve 1 gram of the metal in 25 c.c. nitric acid (sp. gr. 1.2), and add 25 to 30 c.c. of dilute sulphuric acid (1 in 3). The nitric acid is expelled by evaporation, the residue taken up with water, filtered hot, and the separated silicic acid washed with hot water.

D. B.

**Carbohydrate from the Chemically combined Carbon in Cast-iron, and the Estimation of that Carbon in Cast-iron, Wrought-iron, and Steel.** By J. A. ZABUDSKY (*Jour. Russ. Chem. Soc.*, 1882, 3).—On treating Swedish "spiegeleisen," free from manganese, graphite, sulphur, or phosphorus, and containing 4.104 per cent. of combined carbon and 0.23 per cent. of silicon, with cupric chloride (a mixture of copper sulphate and sodium chloride), the combined carbon is converted into and separated as a dark-brown body, having the composition of a carbohydrate. The analysis corresponds with the formula  $C_{12}H_6O_3$ , and a similar body was obtained on decomposing cast-iron by chloride of silver or by electrolysis. On gently heating it with common nitric acid, the carbohydrate is converted into a cinnamon-red nitro-compound, easily soluble in nitric acid. This explains the red colour of the nitric acid solution of cast-iron when the combined carbon is estimated by Eggertz's colorimetric method. The compound contains 53.71 C, 2.95 H, 2.90 N, and 40.44 O (by difference). A nitro-compound of different composition was obtained in a similar way from Bessemer steel. The author obtained halogen-derivatives of the above carbohydrate, e.g., the iodine compound,  $C_{60}H_{28}IO_{15}$ .

For the determination of combined carbon in cast-iron, wrought-iron, and steel, the metal is dissolved in a solution of copper sulphate and sodium chloride. The precipitated copper is dissolved either in the same liquid or in ferric chloride. The combustible part of the residue contains 65 to 72 per cent. of combined carbon, according to the purity of the metal. As the result of many analyses, the author gives the following coefficients for carbon in that residue:—0.715 for "spiegel," free from manganese; 0.685 for manganese-spiegel; 0.70 for white iron and pure grey iron; 0.655—0.675 for different kinds of soft steel; 0.675 for hard steel; 0.690 for wrought-iron. The coefficients, 0.67 for all kinds of steel and iron, and 0.70 for all kinds of "spiegeleisen," may be used as approximately true. The author considers his method more accurate and practicable than Eggertz's iodine process.

B. B.

**Solubility of Silver Chloride in Water.** By J. P. COOKE (*Chem. News*, 44, 234—236).—During the analysis of antimonious chloride, it was noticed that on adding the washings (warm water) of the silver chloride precipitate to the filtrate, it became turbid. This solubility of silver chloride has been examined by Stas, whose results the author confirms and extends. The chloride is most soluble when

flaky, but on continued washing with hot water it becomes pulverulent and insoluble.  $1\frac{1}{2}$  grams of silver chloride washed with about 60 litres of boiling water loses about 15 per cent. of its weight, only about 1 mgrm. becoming reduced. The same result is obtained on using acidified water, viz., from 5—200 c.c. of nitric acid ( $\rho = 1.355$ ) per litre. If the wash-water contains a little silver nitrate, its solvent action is diminished, and with 1 decigram per litre is *nil*.

A wash-water just acidified with hydrochloric acid has a greatly diminished solvent action, but the latter cannot thus be entirely corrected. That the water acts simply as a solvent is shown by a considerable portion separating out on cooling, and this in most minute cubes. It was found that 1 litre of boiling water shaken or boiled for one hour with an excess of precipitated silver chloride gave with silver nitrate 0.0020, and with hydrochloric acid 0.0009 gram of precipitate. To show the influence of this solubility, two series of four determinations of the chlorine in antimony chloride were made, washing in the first with boiling distilled water, in the latter with hot water containing 0.01 per cent. silver nitrate, finally washing with cold water only. 1st series, mean per cent. of chlorine 46.422, with maximum difference from mean 0.047; 2nd series, 46.634, with a maximum difference from mean of 0.017; difference between means of two series 0.212. By this simple device, the advantages of washing with hot water may be secured, whilst its solvent action is prevented. The effect of this solvent action on the author's recent determination of the atomic weight of antimony is discussed. The solubility of silver bromide is almost too small to allow of its estimation; in cold or tepid water it is practically insoluble, but in boiling water is not more soluble than silver chloride is in cold water. For the determination of atomic weights, the analysis of a bromide can be much more accurately carried out than that of a chloride.

H. B.

**Electrolytic Determination of Copper and the Formation and Composition of so-called Allotropic Copper.** By J. B. MACKINTOSH (*Chem. News*, **44**, 279—281).—When the copper is precipitated from a nearly neutral solution of the nitrate in presence of a small quantity of an organic acid, the results obtained are always higher,—on the average 1.25 per cent.,—than when a solution of the nitrate is used. This excess is due to the reduced metal containing carbon, hydrogen, and nitrogen, viz.:—

C.	H.	N.	Cu.
0.74—0.95	0.06—0.12	0.19—0.20	96.85 = about 98.00.

The remaining 2 per cent. is probably oxygen; but no cuprous oxide is present. Allotropic copper prepared according to Schützenberger's method by the electrolysis of the acetate, was found to contain C per cent. 0.42—0.47, and H per cent. 0.09—0.10; this copper is very porous and brittle, and on standing or warming to 100° in the air, it absorbs over 2 per cent. of oxygen, and, according to Schützenberger, contains 5—10 per cent. of cuprous oxide. The metal prepared from a solution of the nitrate containing citric acid, &c., is quite stable in the air.

Considering the fine state of division of the "allotropic" copper and the presence of organic compounds therein, the author thinks that the anomalous reactions can be sufficiently explained without assuming the existence of a new form. Also the deposition of the copper for analytical purposes must take place from the solution of the sulphate, and not from the nitrate with addition of organic substances.

H. B.

**Detection of Fusel-oil in Spirit.** By A. JORRISOW (*Bied. Centr.*, 1881, 791).—One-tenth per cent. of fusel-oil can be detected in spirit by the addition of 10 drops of colourless aniline, and 2 to 3 drops of sulphuric acid, to 10 c.c. of the spirit: a red coloration is produced. If less than 0.1 per cent. is present, then a greater quantity of the spirit must be shaken up with chloroform, and the test applied to the residue after evaporation of the chloroform.

E. W. P.

**Detection of Starch-sugar Syrup mixed with Sugar-house Molasses.** By P. CASAMAJOR (*Chem. News*, 44, 265).—A quantity of the syrup is stirred with three times its volume of strong methyl alcohol ( $93\frac{1}{2}^{\circ}$  Gay-Lussac's alcoholometer). A genuine sugar-house syrup when treated in this way will dissolve with the exception of a very slight turbidity, which remains suspended; if, however, it contains any admixture of starch-sugar it is very turbid, and when left at rest separates into two layers, the lower being a thick viscous deposit containing the glucose syrup. Some thin syrups when treated in this way deposit hard sugar crystals, which, however, cannot be confounded with the above. Ethyl alcohol of the above strength cannot be used, as genuine syrup does not dissolve in it. The adulteration may also be detected by combining the determinations of sp. gr. and of rotary power, or of reduction with the copper test.

H. B.

**Action of Gluconic, Saccharic, Lactonic, and Mucic Acids on an Alkaline Copper Solution.** By H. KILIANI (*Ber.*, 14, 2529—2530).—Fehling's solution is not reduced by gluconic, saccharic, lactonic, or mucic acids.

W. C. W.

**Estimation of Free Acids in Animal and Vegetable Fats.** By F. STOHMANN (*J. pr. Chem.*, 24, 506—512).—The author finds Burstyn's method inefficient. It consists in shaking the fat with an equal (or double) volume of 90 per cent. alcohol; the acids are supposed to be taken up, and the oil to be left perfectly free from acid. In this paper it is shown that the oil retains a considerable quantity of acid even after repeating the treatment with alcohol six times; and further, that this residual oil (or an oil poor in acids) will even absorb stearic acid from its alcoholic solution when shaken with it. The undermentioned modification of F. Hofmann's method is recommended as efficient: to 10 grams of oil (or solid fat, dissolved in ether), 100 c.c. of 96 per cent. alcohol, of known acidity, is added: the whole is then titrated with standard barium hydrate solution (7 grams  $\text{Ba}(\text{OH})_2$  to 1 litre), a few drops of a neutral solution of rosolic acid being used as indicator.

D. A. L.

**Examination of Turkey-red Oil.** (*Dingl. polyt. J.*, **242**, 454.)

—To determine the percentage of fatty acids, Brühl agitates 50 grams of the oil to be examined with 20 grams dilute sulphuric acid (1 in 10), and extracts the sulpho-ricinoleic acid with 30 c.c. ether: 61.9 per cent. of this acid was obtained.  
D. B.

**Supposed Reagent for Distinguishing Ptomaines from Vegetable Alkaloids.** By P. SPICA (*Gazzetta*, **11**, 486—487).—Brouardel and Boutmy have proposed to use potassium ferricyanide to distinguish between ptomaines and the natural alkaloïds, stating that it is reduced by the former, but not by the latter. The author, however, shows that the ferricyanide is reduced by many of the vegetable alkaloids, such as strychnine, brucine, veratrine, nicotine, conine, morphine, and narceine. With atropine, quinine, and cinchonidine, the reduction takes place slowly, and is but feeble.

C. E. G.

**Titration of Cœnolin and Cœnotannin in Wine.** By F. JEAN (*Compt. rend.*, **93**, 966—969).—The colouring matter of wine, like tannic acid, decolorises iodine solution, 100 parts of tannin corresponding to 61.7 parts of the colouring matter (cœnolin). On this fact the author bases a method for the titration of the colouring matter in red wine.

3—5 c.c. of a saturated solution of sodium bicarbonate are added to 10 c.c. of the wine, and the latter titrated with iodine. The end of the reaction is indicated by a method described in the paper. The colouring matter from another portion of the wine is then extracted with ether, and the dissolved cœnotannin titrated with iodine. The difference between the quantity required in the first and second operation gives the cœnolin. Wines coloured artificially with campeachy, cochineal, &c., which also act upon iodine solution, should be treated with tannin (0.1 gram to 10 c.c.), whereby the colour of the wine becomes considerably brighter.

T. C.

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### Technical Chemistry.

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**Dowson's Apparatus for making a Cheap Gas for Gas Motors.** (*Dingl. polyt. J.*, **242**, 449.)—By means of the following apparatus, a powerful gas of regular constitution is said to be produced:—The retort or generator consists of a vertical iron cylinder, which is covered internally with a bad conductor of heat, so as to avoid loss of heat and oxidation of the metal. At the bottom of this cylinder there is a grate to receive the fire, under which a closed chamber is placed. Into this a stream of superheated steam passes, carrying with it a continuous current of air. The steam pressure forces this mixture of steam and air upwards through the red-hot fuel; thus the combustion is maintained and the steam decomposed.

The evolution of gas in the generator is constant, and the quality of the gas regular. The gas obtained is a mixture of hydrogen, carbonic oxide, and nitrogen, with a small percentage of carbonic acid, which has escaped decomposition. It is best to use anthracite coal as fuel. For gas motors, it is not requisite to purify this gaseous mixture. The gas burns with a smokeless flame and deposits no soot.

D. B.

**Preserving Wood by means of Copper Sulphate.** (*Dingl. polyt. J.*, 242, 444—446).—De Lafolaye describes Boucherie's method of preserving wood by forcing a solution of copper sulphate into the timber, especially with reference to the preservation of telegraph poles cut from resinous wood. A series of experiments was made with a view of determining the change which copper sulphate suffers when injected into green wood, seasoned wood, and wood in different stages of decay. Green wood absorbs large quantities of copper sulphate, which gradually disappears on using the wood without altering its constitution. This observation leads to the assumption that the free salt *per se* is not the preserving medium, but that the antiseptic action is brought about by a certain quantity of copper sulphate having combined with the wood cells. This circumstance does not apply to wood in a partial state of decay; such wood when used not merely loses all its free copper sulphate, but the quantity of combined salt diminishes in accordance with the progress of the process of decomposition. As to the preservation of telegraph poles, it is mentioned that young trees are more easily and efficaciously preserved than older trees.

D. B.

**Preparation of Chlorates.** (*Dingl. polyt. J.*, 242, 454).—On decomposing the product of the action of chlorine on milk of lime with potassium chloride, part of the potassium chlorate on crystallisation remains in the calcium chloride mother-liquor, and cannot be recovered. Pechiney diminishes this loss by removing the greater portion of calcium chloride previously to the decomposition with potassium chloride. This is effected either by concentrating the solution and crystallising out, or adding calcium oxide. It is best to use both methods one after the other. On heating, basic chlorides are obtained, which are separated from the liquor. They contain large quantities of calcium chlorate, and are decomposed by hot water. The solution of calcium chloride and chlorate is then evaporated, after the separation of the lime. This mixture is capable of yielding larger quantities of potassium chlorate than the ordinary method. For the preparation of sodium chlorate, sodium sulphate is used, the calcium oxide remaining in solution being separated with sodium hydroxide.

D. B.

**Extraction of Metallic Zinc from its Solution by Aid of the Electric Current.** (*Dingl. polyt. J.*, 242, 390).—According to Luckow, the form in which the separation of metallic zinc takes place when an electric current is passed through a neutral solution, depends on the concentration of the latter and the power of the electric current. With an increase of both, the reguline form of the separated

metal is transformed more and more into the granular and even fine-grained form, the size and distance of the poles being the same in all cases. Hence it is necessary to use concentrated zinc solutions containing as much as 20 to 30 per cent. zinc. The decomposition is effected in square boxes, made of wood or earthenware, the dimensions being 1 to 1.2 m. high, about 1 m. wide, and 3 to 4 m. long. As cathodes, zinc plates or latticed boxes filled with coke are used; as anodes, mixtures of zinciferous ores, with or without coke placed in latticed boxes, or coke alone may be used.

D. B.

**Purification of Arsenical Copper.** By J. GARNIER (*Compt. rend.*, **93**, 1148—1149).—The author employs a basic hearth, consisting of a mixture of lime and pitch, and over this a false hearth of limestone, mixed with manganese dioxide, which is renewed at each operation. The furnace is then charged with the copper, and during fusion the limestone and manganese dioxide become heated and evolve carbonic anhydride and oxygen, which permeate the semi-fluid metal, stirring it up and oxidising it. When the metal become sufficiently fluid, the lime and protoxide of manganese rise to the surface, traversing the molten metal and uniting with most of the arsenic acid.

To remove the last traces of arsenic, the copper is allowed to cool until pasty in a current of air, and is then remelted with a further addition of basic slag.

A sample of copper from Rio Tinto gave the following result:—

	Arsenic per cent.	Iron per cent.
Copper .....	0.789	0.320
After 1st fusion.....	0.141	0.022
" 2nd   " .....	0.113	traces
" 3rd   " .....	0.023	—

This method renders roasting unnecessary, and the almost complete absence of silica diminishes the loss of metal in the slag.

L. T. O'S.

**Brewing in Japan.** By R. W. ATKINSON (*Chem. News*, **44**, 230—233).—The process consists first, in the preparation of "kôji," which corresponds to our malting; and secondly, in the conversion of this by fermentation into "saké." The grains of rice are deprived of the husk, testa, and embryo, steamed for about one hour, thrown on straw mats, and allowed to cool. At about 26° C., a small quantity of the spores of a mould is mixed with a little of the rice, the mixture scattered over the remainder, and well mixed with it by hand. It retains its temperature for 24 hours, after which it is placed on shallow wooden trays, transferred to underground chambers, kept at 26°, and provided with a slow circulation of air. The mass heats up to 41°, the spores throwing out filaments of mycelium, whilst oxygen is absorbed and carbonic anhydride abundantly formed. By this time the mass has become matted together, when it is cooled by spreading it out, again collected into heaps, and allowed to heat, after which the kôji, as the rice has now become, is spread out and allowed

to completely cool. The rice (dry) used loses about 11 per cent. of its weight.

*Insoluble in Water.*

	Starch.	Cellulose.	Fat.	Ash.	Albuminoids.
Whitened rice dried at 100°.....	82.27	4.79	0.49	0.46	7.50
Kôji dried at 100°..	56.00	4.20	0.43	0.09	1.50

*Soluble in Water.*

	Albuminoids.	Dextrose.	Dextrin.	Ash.	Water.
Whitened rice dried at 100°.....	1.95	1.91		0.63 = 100.00	12.70
Kôji dried at 100°..	8.34	25.02	3.88	0.52 = 99.98	25.82

The percentage of starch calculated from the amounts of starch, dextrose, and dextrin present in the kôji amounts to 82.4, agreeing with that present in the original rice. A cold decoction of kôji renders thick starch-paste quickly liquid, especially at about 45°. If the kôji is digested with water 3—4 hours at 50—55°, almost the whole of the starch goes into solution as dextrose. Unlike malt extract, kôji can convert maltose into dextrose. The materials used in mashing and fermentation consist only of steamed rice, kôji, and water. A mash is made of steamed rice 2 bushels, kôji  $\frac{3}{4}$  bushel, and 16 gallons of water, and kept between 0—5° for several days; this is always done in the winter. It is then warmed, when fermentation sets in, and continues for several days, the temperature rising to about 23°, when it is cooled. It then contains about 10 per cent. alcohol, but the object of this fermentation is rather to produce a ferment which in the second stage will cause the rapid conversion of dextrose into alcohol.

	Alcohol.	Dextrose.	Dextrin.	Glycerin, ash, and albuminoids.
Mash just before heating on the 5th day .....	—	12.25	5.69	0.48
After heating, 7th day ..	5.20	5.40	7.00	1.14
„ „ 14th day..	9.20	0.50	2.57	1.93
	Fixed acid.	Volatile acid.	Water by diff.	Calculated starch undissolved.
Mash just before heating on the 5th day .....	0.019	0.008	81.553	20.43
After heating, 7th day ..	0.310	0.150	80.800	10.68
„ „ 14th day..	0.300	0.030	85.470	12.05

The percentage of starch in the rice used was 32.17; subtracting from this an amount corresponding with the amounts of alcohol, dextrose, and dextrin formed, the percentage of “starch undissolved” is found. This mash is now mixed with fresh quantities of steamed rice, kôji, and water; the fresh kôji is required to bring the starch of the rice into solution, since that added in the preparation of the mash is ex-



hausted; and as fast as the starch becomes converted into sugar, it is acted on by the ferment of the mash, and converted into alcohol and carbonic anhydride. Thus, unlike the English brewing, the amount of alcohol may be very largely increased by successive additions of rice and kôji.

After fermentation, the mash is filtered, the tuns are rinsed with water, and this is added to the rest of the brew, thus slightly lowering its strength. The alcohol contained in the insoluble residue is obtained by distillation. The yield is not much more than 50 per cent. of that theoretically obtainable from the starch. There is no great variation in the composition of this saké; it differs markedly from beer in the very minute proportions of dextrose and dextrin which it contains.

	Alcohol.	Dextrose.	Dextrin.	Glycerin, ash, and albuminoids.
(1.) Lowest .....	11.00	0.200	0.14	1.580
(2.) Highest .....	13.73	0.404	0.18	1.833

	Fixed acid.	Volatile acid.	Water by diff.	Sp. gr.	Specific rota- tory power.
(1.) Lowest .....	0.130	0.014	86.936	0.991	20.6
(2.) Highest ....	0.143	0.026	83.684	0.989	24.0

During the hot summer months, the beer requires to be continually watched, and heated about once a month, in order to keep it from turning.

H. B.

**Treatment of Wine Casks.** By NESSLER (*Bied. Centr.*, 1881, 636—637).—The author thinks the ordinary mode of sulphuring empty wine casks not effective. Many germs of mould escape destruction in the process, and, if it is frequently repeated, sulphuric acid forms and attacks the wood; the casks should be well rinsed with cold water between each operation; hot water produces ill-smelling and tasting bodies. He considers washing with sulphuric acid,  $\frac{1}{4}$  pound in 1 hectolitre water, the most effective cleanser. J. F.

**Effect of Gypsum on the Constitution of Wine.** By KAISER (*Bied. Centr.*, 1881, 632—633).—According to Griessmayer, when gypsum is added to the must, it forms with the tartar present neutral calcium sulphate and free tartaric acid, which latter reacts on the sulphate, forming bitartrate and acid calcium sulphate. The ash of such wine is neutral, and does not give out carbonic acid when treated with hydrochloric acid. When gypsum is added to the finished wine, the alcohol prevents its solution, but it carries down many impurities. The author's experiments were undertaken to test the value of these conclusions. He found that the calcium bitartrate became bisulphate, and the total tartaric acid became insoluble as a neutral calcium tartrate. In the finished wine, by the addition of gypsum, the tartaric acid is replaced by sulphuric acid, and there is a perceptible increase in the calcium, the other contents remain unaltered. From the proportions of the ash to the extractive matter, the author is able to

declare with certainty whether the wine has been plastered as must or finished wine; in the first case the ash is disproportionately high; in the other it remains normal.

As to the question whether a plastered wine should be called adulterated, the author says that an article which, by treatment, is deprived of its most characteristic constituent, tartaric acid, whilst another substance, calcium bisulphate, not normally present, is introduced, cannot be called anything but adulterated. J. F.

**Changes which Lemon Juice Undergoes.** By I. MACAGNO (*Gazzetta*, 11, 443—450).—The author has made numerous determinations of the acidity of lemon juice, and of the amount of citric acid (by Warington's method) in it in various conditions. He finds that the alcoholic fermentation which takes place when freshly expressed lemon juice is kept, does not diminish the amount of citric acid present, but that this is succeeded by another fermentation during which bacteria make their appearance; this causes the amount of citric acid to diminish, and the proportion of other acids—chiefly acetic and propionic—to increase. In like manner, juice expressed from fruit which is partly rotten contains other acids besides citric acid, sometimes as much as 10 per cent. of the total quantity. Comparative experiments made by concentrating portions of the same fresh juice over a water-bath and the open fire, showed that in the latter case there is a considerable loss of citric acid, sometimes as much as 8 to 9 per cent. of the whole, but if the juice has undergone the alcoholic fermentation before being evaporated over the open fire, the loss is not so great; at the same time, a certain quantity of citrates is formed, so that the acidity, as determined by alkalimetric titration, is less than that which would be produced by the citric acid present if it were all free.

The author considers that the ordinary system of analysis based on acidimetry usually gives erroneous results, as either more or less citric acid may be present than is indicated by the acidity. Warington's method of determining the citric acid as calcium citrate, although open to objections from a scientific point of view, is both convenient and sufficiently accurate for commercial purposes. C. E. G.

**Oil of Anda-Assu.** (*Pharm. J. Trans.* [3], 12, 380.)—This oil is obtained from the seeds of the *Johannesia princeps*, Vell., a large tree of Brazil, of the natural family Euphorbiaceæ. The seeds have long been used as a purgative. By expressing 50, weighing about 350 grams, about 48 grams of a fine clear slightly yellowish odourless oil is obtained. Its taste is at first somewhat nauseating, afterwards saccharine. It dissolves in ether, oil of turpentine, and benzene, solidifies at 8° (sp. gr. 0.9176 at 18°).

M. Olliveira found 0.4 per cent. of an active principle, which he calls Johannesine, in the seeds. The oil produces the same degree of effect as castor oil, with a smaller dose, and it has not the repulsive odour of the latter. A gripping principle seems to reside in the embryo, and in the skin of the seed; both of these should, therefore, be removed when making an emulsion of the seeds. F. L. T.

**Cotton-seed Oil.** By E. SCHEIBE (*Chem. Centr.*, 1881, 703).—The author has examined a sample of pure cotton-seed oil, and finds it suitable for many purposes for which olive oil is used. The oil at ordinary temperatures is clear, transparent, and of a golden-yellow colour, of mild taste and without smell; sp. gr. = 0.923. The oil does not belong to the *drying* class, although it gives imperfectly the nitrous acid reaction (elaidic acid test); it does not, however, give a green coloration with acids or alkalis; with concentrated sulphuric acid, it gives a dark-brown coloration. It solidifies at 1°, is readily saponified with caustic alkalis or lead oxide; with ammonia, it forms a good liniment. Towards solvents (ether, benzene, &c.) it behaves as *salad oil*.

From these properties it is easy to sophisticate commercial *salad oil* with the cheaper cotton-seed oil; or even to substitute the one for the other; but the presence of the latter is revealed by the imperfect elaidic acid reaction, its sp. gr. its solidifying point, and its ready and complete solidification.

V. H. V.

**Researches executed in 1880 at the Dairy Station of Fan (Cantal).** By E. DUCLAUX (*Ann. Agronomiques*, 7, 255—285).—In this paper, the author discusses the observations made during 1880 in connection with the general results of his previous researches, on the part played by microscopic organisms in the ripening of cheese (*ibid.*, 4, 5; 5, 5; 6, 161).

Having previously described in detail the life history of a few of these organisms, he has now, by partial study of a greater number of species, generalised the chief conclusions which he had drawn.

These microscopic organisms develop at the expense of the casein, the fat remaining unaltered, except as the result of a secondary action, viz., saponification by the carbonate of ammonia, which is an ultimate product of the alteration of some of the casein; a little of the glycerol thus liberated may also ferment. These secondary changes are inconsiderable in amount and in effect on the former. The casein, which serves as the nutriment of the ferments, is by them resolved into a descending series of groups of decomposition-products. These include soluble albuminoids; alcoholic extractives; crystallisable compounds like tyrosine, leucine, alanine; acetate, butyrate, valerate and other ammonium salts of the fatty acids, and finally, ammonium carbonate, which renders the ripened cheese feebly alkaline. It is to the various mixtures of these direct products of the action of the ferments that the flavours of the various cheeses are due; their amount, however, bears but a small proportion, like that of a condiment, to the mass of alimentary material, which has a different origin.

The living cells of the microscopic ferments secrete bodies of the nature of *diastase*, which have the properties of chemical reagents, and effect decompositions in the casein throughout the mass of the cheese, the living cells from which they originated existing only on the surfaces in contact with air. These diastases are of two kinds: a variety (like rennet) which coagulates milk, but cannot bring about the re-solution of the coagulum, and a second variety (resembling the pancreatic ferment) which can digest and dissolve the precipitated casein. It is

this second variety which plays the chief part in the ripening of cheese, the coagulated casein being invariably produced by the action of rennet. The digestive diastase can transform curd in a few days into products having the appearance and consistency of *brie* or *camembert* cheese, but quite insipid, since they lack the flavouring constituents which have been enumerated above as the direct products of the growth of the microscopic organisms.

*Rennet Diastase.*—The coagulating diastase resulting from the living ferments of cheese being similar to rennet diastase, a study of the latter will disclose the properties common to both. The active portion of rennet prepared in the ordinary manner is the dried mucous membrane forming the interior lining of the calf's stomach. The external muscular coat, and the granules of coagulum found in the stomach are also impregnated with it to a less extent. These granules of curd contain numerous microscopic ferments, which as soon as the calf is killed, and during the days taken up by the drying of the rennet, secrete the active diastase of the rennet. The coagulation produced by the rennet is therefore effected in the same manner as that sometimes brought about by the use of a piece of old cheese. The multiplication of the microscopic ferments and the consequent increase of diastase continue during the maceration of the rennet, so that the liquid, with additions of water or skim milk in place of the portion removed daily for use, retains its coagulating power until the appearance of putrefactive organisms, when it is thrown away and a fresh maceration made. Solutions of rennet diastase thus made have no constant coagulating power; it is almost nothing at first, begins to be well marked in 24 hours' time, and then reaches a maximum, and gradually declines. The concentrated solutions found in commerce ("essence of rennet"), like that of Hansen of Copenhagen, are much more uniform, and 1 litre of these will coagulate 10,000 to 15,000 litres of milk. The method of preparation is kept secret, but a similar and very active rennet essence may easily be prepared as follows:—The stomach of a young calf is washed rapidly with plenty of water, distended, and exposed to the air for two or three months. The part next the pylorus is removed, the remainder cut up into small pieces and macerated for two or three days in 6 times its weight of a 5 per cent. solution of salt; 5 per cent. of salt and 10 per cent. of alcohol (or 5 per cent. boric acid) are now added, the clear liquid decanted, the remainder filtered, and the filtrate mixed with the decanted portion. It is not absolutely necessary to take a calf living entirely at the udder; the rennet diastase persists for eight or ten months, being gradually replaced by pepsine. Rennet essence, however prepared, must be preserved in the dark, in full bottles, tightly corked. By adding 7 or 8 times its volume of alcohol to rennet essence, a mass of mucus is precipitated which carries with it all the diastase. The precipitate may be filtered off after 12 hours (not more), and dried at a gentle heat. In this state it resists well the action of the air, and may be dissolved in water when required for use.

The ordinary temperature of coagulation is 25–35°; at 65° the diastase is destroyed; at 10° pure rennet may be left in contact with sterilised milk for an indefinite time without causing coagulation;

at 41° the maximum effect is produced, whilst the temperature of milk as it comes from the cow is 37°. The coagulation power of a preparation of rennet may be expressed by the quantity of milk which 1 c.c. of it can coagulate at 37° in 45 minutes (a period commonly allowed). The time required for coagulation is inversely proportional to the quantity of rennet employed, provided that the former is not much less than 20 minutes or more than 60 minutes, and the latter neither too large nor too small. Under favourable conditions, 1 part of dry mucus will cause the coagulation (in 45 minutes at 37°) of 200,000 parts of milk; to produce this effect, the mucus need not contain more than 10 per cent. of diastase. The coagulative power of the diastase from the living cheese ferments is not so easy to estimate as that of rennet, nor is the simple inverse relation between the quantity employed and the time of action so apparent; this is due to the fact that the digestive diastase is also present, and begins to exercise a solvent action on the coagulum as soon as it is formed. Like rennet diastase, however, the cheese diastase can cause the coagulation of an extremely disproportionate quantity of milk.

*Digestive Diastase.*—This coexists with the rennet diastase in all the microbia examined by the author, but in variable proportion, and the effect produced on milk will vary with this proportion, with the nature of the microbia, with the supply of air, and with the temperature. For example, clubbed vibriones (anærobia) sown in milk in a deep tube, in 48 hours, produce a white, firm, very opaque coagulum; re-resolution of this coagulum will commence by the aid of the digestive diastase produced, but will be very slow, and perhaps never complete. On the other hand, if the ærobia which the author calls *filamentus tenuis*, be sown in milk in a shallow vessel at a temperature under 20° C., no coagulation will take place: the milk loses its opacity gradually from the top downwards, and in 48 hours has the appearance of whey; at 30° or 35°, the same organism always produces coagulation, not because there is more rennet diastase produced, but because the temperature is more favourable to its action. Between these two extremes, all the other cases are comprised. With ærobia, generally, the coagulum, when produced, is of short duration.

The diastases can be separated from the microbia which have produced them by adding alcohol to the solution; this precipitates the diastases. The precipitate placed in contact with a fresh portion of milk, enables the action of the diastase on milk to be studied apart from that of the microbia. The diastases from all species of microbia ultimately convert milk into solutions differing amongst themselves no more than do specimens of casein from different samples of milk. This liquid remains amphoteric like normal milk (*i.e.*, it blues red litmus and reddens blue litmus). The soluble albuminoid into which the casein has been transformed is not precipitated by ebullition, nor by lime-water in the cold.

Baryta-water produces whitish flocks; copper sulphate, bluish flocks; mercuric chloride an abundant turbidity; potassium ferrocyanide produces no precipitate; acetic acid produces a very slight precipitate. The milk is in fact incoagulable by acids, and its casein has become a true peptone. Bearing in mind the action of diastase on

starch and other bodies, the author thinks it may here also be a hydration, perhaps accompanied by polymerisation. The author points out the bearing of these results on the digestion of milk. The casein is coagulated by the rennet diastase in the stomach of the young mammal, by the acid gastric juice in that of the adult. It cannot be again rendered soluble until the acid reaction has been neutralised by the bile, when the digestive diastase of the stomach and that of the pancreas come into play, and produce re-solution. This explanation justifies the common remark that a well-matured rich cheese is a half-digested food. In the intestines, where the reaction remains neutral or alkaline, microbia may flourish, and by producing more digestive diastase still further assist digestion; this is proved by the presence in digested food of ammoniacal salts of fatty acids, leucine, tyrosine, &c. (even when cheese has not been eaten), which are not products of the action of diastases on albuminoids, but of the direct action of microbia.

*General Theory of Cheese-making.*—Milk, even when just drawn from the cow, contains living organisms, derived from contact with the udder, the hands of the milker, or the vessel in which it is received. These are *aërobia*, which deprive the air of its oxygen, and produce diastases which coagulate the casein. A few drops of indigo carmine, added to new milk in a full corked phial, soon lose their colour, which is restored on opening the phial and pouring the milk through the air. The time taken for this decoloration may be used as a rough test of the keeping quality of the milk. Coagulation takes place in two ways. It is generally preceded by transformation of milk-sugar into lactic acid by the lactic ferment, which is found in the liquid as turbescent particles, varying in length and size. Neutralisation with a few drops of sodium bicarbonate, and ebullition, destroy the ferment and prevent coagulation. Borax is frequently added for this purpose. But milk may also coagulate whilst remaining neutral, or even slightly alkaline: in this case it is not brought about by the lactic ferment, but by *aërobia* acting as casein ferments and active producers of diastases; ebullition, even with addition of sodium bicarbonate, does not always arrest this coagulation. These ferments are most active at 40–45°, and if the milk can be heated to this point without coagulating, then on raising the temperature to 100°, the ferments will be destroyed.

Milk for cheese-making is either taken just as it comes from the cow, at a temperature of 35–37°, or, if it has been allowed to cool, it is warmed up to this temperature; the living organisms which it contains, therefore, multiply under favourable conditions up to the moment of coagulation, when they become entangled in the curd, and accompany it throughout subsequent operations. To make fine cheeses, but little rennet is added; the coagulation takes a long time, and the curd remains soft, and retains much whey. It is drained slowly, and as perfectly as possible, in order to get rid of the milk-sugar, which is partly oxidised and partly converted into lactic acid, rendering the curd temporarily acid. The casein ferments then develop on the surface, giving rise to ammonium carbonate, which neutralises the lactic acid, and ends by rendering the curd alkaline: at the same time they give rise to diastases, which penetrate the cake little by little, and

a yellow translucent layer, gradually advancing to the centre, takes the place of the white opaque casein. The different varieties of cheese are matured by diastases proceeding from different ferments, and the skill of the manufacturer consists in utilising always the same ferments, and preventing the invasion of others. The useful ferments are generally present in much larger quantities than the others, for they impregnate the air of the factory, the vessels, the ground, and the clothing of the operatives. Long routine has taught the conditions most favourable for their development, but if these conditions are temporarily lacking, a neighbouring species may establish itself, incapable of producing the particular kind of ripening desired. The cellar is then said to be sick, and the manufacture has sometimes to be abandoned for a time, to be resumed at a more favourable season. Besides the ferments already mentioned, *moulds* (mucedineæ), and *torulaceæ*, also assist in the ripening. Both of these live only on the surface exposed to the air, the former existing as vegetative masses composed of mycelium, organs of nutrition, and reproductive organs, the latter consisting of autonomous cells grouped together in greasy masses. They both produce a rennet diastase and a digestive diastase, identical with those produced by the other ferments, but as these moulds and *torulæ* live only on the surface, they are more easily affected by variations of temperature and humidity, and the manufactures which make use of them are more uncertain than the others.

Roquefort and Pontgibaud cheeses and many others are ripened by means of the mould *Penicillium glaucum*. It is cultivated at a temperature as near 0° as possible, not because this is most favourable to its development, but because the development of other species, especially of vibriones, is thus hindered. Since cheese is not a favourable medium for its growth, its increase is encouraged by copious sowing of mouldy bread. In order that it may spread throughout the cheese air is admitted to the interior by piercing fine holes.

In making Gruyère cheese the principal difficulty occurs in heating the curd (to about 50°), which is done to expedite the elimination of the serum, in order that the curd may be immediately pressed in a mould. If the granules are too large and the heating too rapid, an impermeable coating is produced in the press, through which the serum cannot escape. Hence the utility of slow heating and constant stirring, which causes it to *grain well*. The grains should be yellowish, not adhering when pressed between the fingers, and should crumble when mashed. The curd still contains a little milk-sugar, which is got rid of by fermentation. The most common ferment is like an elongated 8, which multiplies only by division in the centre. When young, it is surrounded by a gelatinous layer, which also divides and surrounds each new individual. This layer disappears in the old specimens, leaving them naked and isolated, and resembling the particles of lactic ferment. This ferment resolves sugar of milk into several products, amongst which are alcohol, acetic acid, and carbonic anhydride, and the carbonic anhydride thus produced gives rise to the vacuoles in the cheese. The ferment is killed at a temperature very near 50°, but varying with the acidity or alkalinity of the curd, and therefore if the curd is overheated, the cheese becomes dry, and ripens with difficulty,

and is said to be dead. If the curd is undercooked, too much milk-sugar is retained, fermentation becomes very active, too much gas is disengaged, causing the vacuoles to become confluent, or a multitude of small channels to appear, when the cheese is called *mille trous*, and loses its value. In a well-cooked curd vacuoles are produced in proper quantity, and when the milk-sugar has disappeared, the ferments very slowly ripen the cheese. Between the cheeses in which fermentation commences at once and proceeds with rapidity, and which should be consumed directly they are ripe, and cheeses such as Gruyère, in which the maturation is rendered as slow as possible, come numerous soft and uncooked cheeses like that of Cantal.

To make Cantal cheese, the milk is rapidly curdled, and the curd so treated, without any heating, as to retain about half its weight of serum. It is not immediately pressed, but submitted to a previous fermentation, which causes the milk-sugar to disappear entirely, and the casein to undergo a curious molecular transformation. If pressed before this fermentation, the casein loses nearly the whole of the water, but retains the fat, and if made from skimmed milk, the mass produced is so hard that buttons can be made of it. After the fermentation, on the contrary, the curd easily loses under pressure a portion of its liquid, but retains the remainder (about half its weight) so obstinately that under a greater pressure the fat is forced out in preference. A prodigious number of organised ferments is forced out with the liquor escaping from the press, but many still remain in the curd, together with the diastases which they have given rise to, and produce a maturation less rapid than that of the fine cheeses, but more rapid than that of Gruyère cheese. The Cantal cheeses have two disadvantages: they mature too rapidly, and the ripe condition is not lasting, being succeeded by a slow depreciation, brought about by the development of *anaërobia*, which find congenial conditions in the large proportion of moisture and the massive size of the cheese.

*Poor Cheeses of Cantal.*—Since the odour and flavour of cheese is due almost entirely to the alteration-products of the casein, and not of the fat, it occurred to the author that cheeses having the character of Cantal cheese could be prepared from partially skimmed milk, and that if this were done they could be more completely deprived of water in the press, and would possess good keeping qualities. He finds that a cheese having the odour and flavour of Cantal cheese can be made from three-fourths skimmed milk and one-fourth entire milk; but the best results are obtained with one-half skimmed milk and one-half fresh milk. Cheeses thus made have not suffered so much alteration in six months as the ordinary Cantal cheese in two months. The process is described in detail. J. M. H. M.

**New Colouring Matters.** (*Dingl. polyt. J.*, 242, 375—383.)—*Preparation of Oxyquinolines.*—According to Skraup of Vienna, 1.4 kilo. of ortho-, meta-, or para-nitrophenol is heated to 130—140°, with 2.1 kilos. of one of the three amidophenols, 6 kilos. glycerol of sp. gr. 1.26, and 5 kilos. sulphuric acid of sp. gr. 1.848. The volatile impurities are driven off by distillation with steam, the residue is neutralised with soda, and the volatile orthoquinoline distilled off with



steam. The other oxyquinolines are extracted from the alkaline liquid with ether.

The preparation of *artificial indigo* has been improved by the *Badische Anilin and Sodafabrik*. By the action of concentrated sulphuric acid on orthonitrophenylpropionic acid at a low temperature, an intermediate product is formed, which gives with iron sulphate a blue colouring matter, resembling indigo, and is precipitated on dilution with water. Instead of iron sulphate, metals may be used, *e.g.*, iron, zinc, tin, lead, copper, bismuth, nickel; further, the lower stages of oxidation, and the corresponding salts of iron, manganese, copper, tin, and other metals; finally metallic sulphides, sulphites, and thiosulphates, potassium thiocyanate, potassium iodide and bromide. The blue colouring matter thus obtained, when treated with sulphurous acid or an alkaline bisulphite, gives a blue solution, from which salt extracts a soluble blue colouring matter; this is converted into another blue insoluble colouring matter on heating or by treatment with acids. For dyeing textile materials, the sulphurous acid derivative, or a mixture of the original blue and a bisulphite is used, and the colouring matter fixed by means of steaming, or by the aid of an acid-bath. The group of alkaline reducing agents, which, like grape-sugar or milk-sugar, effect the transformation of orthonitrophenylpropionic acid, includes the sulphides, sulphhydrates, polysulphides, thiocarbonates, and ethylthiocarbonates of the alkalis and alkaline earths, and especially the alkaline xanthates (ethyldithiocarbonates). The latter act in the cold.

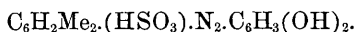
According to Bindschedler and Busch, *tetrazyldiamidotriphenylmethane* and *tetramyldiamidotriphenylmethane* are converted into sulphonic acids, and on subsequent oxidation yield new green colouring matters, resembling the green colouring matters obtained from tetramethyldiamidotriphenylmethane by converting it into a sulphonic acid, and subsequent oxidation. From the condensation-products of salicylaldehyde with dimethylaniline, diethylaniline, and diamylaniline, sulphonic acids, and by subsequent oxidation, new colouring matters are obtained.

*Preparation of Colouring Matters from the Rosaniline Group.*—Greiff proposes to heat 2 mols. aniline or toluidine sulphate or their homologues or mixtures of these bodies with 1 mol. nitrobenzoyl chloride, and 1 mol. ferric chloride or other oxidising agent, to a temperature of 170–200°; a bronze-coloured melt is thus obtained, which, on dilution with water, gives red colouring matters resembling rosaniline. Conrad prepares blue colouring matters from sulphonic acids, formed by the action of ammonium sulphite on nitroso-derivatives of tertiary aromatic monamines.

*Preparation of a Blue Colouring Matter.*—According to Majert, nitroso-dimethylaniline gives the following reaction with thiocarbonic acid:  $3C_6H_4(NO)N(CH_3)_2 + CS(SH_2) = 3C_6H_4(NS)N(CH_3)_2 + CO_2 + H_2O$ . By treating the solution with an oxidising agent, after adding zinc chloride and common salt, a blue colouring matter is deposited in flakes, and a red colouring matter remains in solution. The latter is reduced with zinc and hydrochloric acid, and by renewing the addition of an oxidising agent a blue colouring matter is obtained.

*Preparation of Violet, Blue, and Green Colouring Matters by means of Trichlormethyl sulphochloride.*—Espenschied mixes 1 part methyldiphenylamine with 1—2 parts trichlormethyl sulphochloride, prepared from carbon bisulphide, manganese, and hydrochloric acid, and 5 parts common salt, the mixture being subsequently heated at  $110^{\circ}$ . The copper-coloured melt is treated with water, then alkali is added, and finally concentrated hydrochloric acid. The insoluble base is rendered soluble by sulphuric acid, and worked up in the usual manner. The colouring matter dyes wool and silk blue, with green tinge. The methyldiphenylamine may be replaced by ethyl- or amyl-diphenylamine. When benzyldiphenylamine is used, green colouring matters are produced, which are soluble in alcohol. Violet colouring matters are obtained when diphenylamine or dimethylaniline is used in place of methyldiphenylamine.

*Preparation of New Azo-colouring Matters.*—According to Stebbins orange No. 3 is obtained by diazotising metanitriline and uniting the diazo-compound in molecular proportion with  $\beta$ -naphtholdisulphonic acid in alkaline solution. The colouring matter deposited on adding common salt is soluble in water, and dyes wool orange in an acid-bath. Its composition is  $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{N}_2\cdot\beta\text{C}_{10}\text{H}_4(\text{NaSO}_3)\cdot\text{OH}$ . Orange No. 4 is obtained by mixing equal molecules of paradiazosulpho-xylene with resorcinol in alkaline solution. Hydrochloric acid separates the dye in the form of a red precipitate soluble in water, which in an acid-bath dyes wool golden-yellow. Its composition is



In a similar manner Stebbins obtained the following dye-stuffs:—Parazosulphoxynaphthalene -  $\alpha$  - sulphonyphenol, parazodimethylsulphoxybenzene -  $\alpha$  - naphthol, paradiazosulphoxy -  $\beta$  - naphthol, metazonitrobenzene -  $\alpha$  - naphthol, parazosulphoxylyxylol -  $\beta$  - phenanthrol, parazosulphoxylyxylol -  $\alpha$  - dibromnaphthol, azodinitroxybenzeneparamidosulphoxynaphthalene and parazosulphoxynaphthalene -  $\beta$  naphthol-disulphonic acid.

*For the preparation of dye-stuffs by the action of the halogen on the azo-derivatives of resorcinol*, Bindschedler and Busch azotise resorcinol with nitrous acid, or treat monosodium resorcinolate with amyl nitrite, and heat the nitroso-derivative with resorcinol and sulphuric acid at  $100^{\circ}$ .

Brein obtains new aniline colouring matters by heating to  $170$ — $190^{\circ}$  1 mol. pæonin with 3 mols. aniline hydrochloride. The reddish-violet melt is boiled out repeatedly with acidulated water, then dissolved in dilute soda-ley, and the solution treated with solid sal-ammoniac. A violet-red precipitate is produced. This dye-stuff is said to be an intermediate product between pæonin and the blue (azulin) obtained by Guinont-Marnas and Bonnet by treatment of pæonin (*péonine stable*) with aniline.

By the action of aniline hydrochloride on fluorescein, a new dye-stuff is produced, which may be isolated with dilute soda-ley, having first digested the melt with hot acidulated water. The dye is precipitated by acids. It is not fluorescent, and gives a rose-colour on cloth.

According to the *Badische Anilin und Sodafabrik*,  $\alpha$ - and  $\beta$ -

*naphthylamine*, or their substitution-products, are produced by direct action of ammonia or substituted ammonias on alpha- and beta-naphthol.

*Preparation of Dye-stuffs from Nitro-derivatives of Naphthalene.*—Meister, Lucius, and Brüning in the first place prepare dinitrobromonaphthalene from monobromonaphthalene. By treating the former with eight times the quantity of a mixture of equal parts of sulphuric acid and fuming nitric acid, isomeric tetranitromonobromnaphthalenes are obtained, from which by dissolving in acetic acid or benzene, and boiling with soda-ley, tetranitronaphthol is produced. It forms a yellow dye. The same authors prepare dye-stuffs by the action of disulphonic acids of  $\beta$ -naphthol on diazo-compounds of the aromatic acids.

*Preparation of Dye-stuffs from Sulphosalicylic Acid.*—By the action of nitric acid, sp. gr. 1.35, for 30 hours at 40–50°, the nitro-derivative of sulphosalicylic acid is obtained, which dyes silk and wool yellow without a mordant. Sulphosalicylic acid forms with resorcinol a bronze-red dye, the alkaline solution of which is highly fluorescent. With diazoamidobenzene, sulphosalicylic acid forms a dark Bordeaux-red dye, with diazometaxylidine a magenta-red dye, and with diazoamidonaphthalene a bluish-violet dye. D. B.

**Preparation of Paints.** (*Dingl. polyt. J.*, **242**, 456.)—Scholz's liquid blacking consists of 50 parts asphalte, 50 parts naphtha, 6 parts linseed-oil varnish, 14 parts train oil, and 13 parts spirit of wine.

For the preparation of tannin-black, Cobley and Guard boil leather-waste in a solution of ferric chloride. The dried residue is used as printing ink or as shoe-blackening; in the latter case it is mixed with oil, molasses, or a similar substance.

Bauer obtains a glaze for paper and pasteboard by mixing 100 litres boiling water, 50 grams ultramarine, 1.5 kilos. sodium thiosulphate, 150 kilos. gypsum, and 120 litres of paste prepared from 10 kilos. wheat-starch. The glaze is rendered soft by adding glycerol. Stearin or wax imparts to it a fine lustre.

Hoseman obtains a glue by mixing 50 kilos. calcium chloride solution of 30–32° B., and 25 kilos. potato-starch with 25 litres of water, and warming the mixture to 62–75° with 5 kilos. of an alkaline solution of colophony. 4 kilos. of a mixture of 60 parts tartar, 127.5 parts sulphuric acid of 10° B., and 10.5 parts aluminium sulphate solution of 9° B., and 40 litres water are next added, and the mixture is treated with 1 kilo. zinc chloride solution (10° B.) in 5 litres water and 200 grams phenol with 30 grams nitrobenzene in 4 to 5 kilos. water. The product thus obtained has manifold applications, and forms a substitute for glue and size. D. B.

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## General and Physical Chemistry.

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**Discontinuous Phosphorescent Spectra observed in an almost Perfect Vacuum.** By W. CROOKES (*Compt. rend.*, 92, 1281—1283).—Alumina precipitated from alum by ammonia behaves like the ruby, giving a crimson light and a spectrum which has been already noticed by Becquerel. After having been frequently exposed to electric action, the alumina gradually acquires a permanent rose tint, and presents slight indications of becoming crystalline. In some cases, alumina gives a green phosphorescence; thus the portion which, on precipitation with ammonia, is obtainable only by boiling the solution, and the precipitated alumina obtained from the acetate, give a green and not a red phosphorescence. The author has also met with a specimen of ruby which behaved in a similar manner.

The phosphorescence of glucina is blue; that of zirconia, a very pale blue-green; yttria, dirty green; erbia, yellowish; titanite oxide, deep brown; magnesia, rose; barium dioxide, bright orange-yellow; strontium hydroxide, a fine blue; calcium oxide, bright orange-yellow; potassium hydroxide, pale-blue; sodium hydroxide, yellow; lithium hydroxide, pale-red.

Diamonds exhibit a very brilliant phosphorescence, which is generally blue, but those of the purest water are not the most remarkable in this respect. Diamonds which in sunlight manifest a slight fluorescence, disappearing by the interposition of a yellow glass, phosphoresce very brilliantly of a pale yellowish-green colour.

Many substances seem altogether destitute of phosphorescence; such are the oxides of didymium, iron, chromium, cerium, and thorium, anhydrous baryta and stannic oxide. Thoria appears to possess the power of absorbing gases to an extent greater than that of any other substance; when heated in a vacuous tube, it produces, on cooling, a vacuum so complete that a spark capable of passing over 0.05 mm. in air is stopped by 0.001 mm. in the space thus rarefied.

In almost all the substances examined, a residual phosphorescence remains, which is more or less persistent after the electric current has ceased to act; this is particularly observable in the case of Iceland spar, in which moreover the ordinary and extraordinary rays are found to be polarised in contrary directions.

The author states that his researches have led him to suspect the presence of new elements in some of the materials used, and that he is at present engaged in endeavouring to obtain further and more satisfactory evidence of their existence.

J. W.

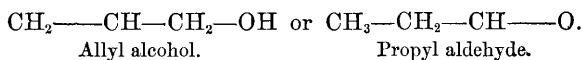
**Relation between the Optical and Thermic Properties of Liquid Carbon Compounds.** By J. W. BRÜHL (*Annalen*, 211, 120—178).—A continuation of the author's researches on the correlation of the physical properties of the carbon compounds and their chemical constitution (cf. Abstracts, 1880, 781; 1881, 15).

The author alludes at the outset to the surmise of Newton that the diamond, owing to its refractive power, is a combustible substance, and to the researches of Dulong and Mohron on the relation between the heats of combustion of gases and their refraction-coefficients. In the present communication, these relations are more fully investigated, and inferences drawn from them with regard to the double linking of carbon-atoms.

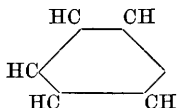
Part I. From determinations of the refractive power made by the author, and the heats of combustion by Berthelot and Louguinine, the following conclusions are drawn:—First, the refractive power and heat of combustion of a compound is decreased by the addition of oxygen, by the removal of hydrogen, or by its replacement by oxygen. This decrease becomes less the greater the number of oxygen-atoms so added or introduced, or in the case of homologues of analogous chemical structure these differences become less with increase of molecular weight. Secondly, the refractive power and heats of combustion are decreased by the replacement of hydrogen by the halogens, or by polymerisation, but are increased in the case of homologous compounds with every  $\text{CH}_2$  grouping added to the molecule, these differences becoming less the higher the molecular weight. Thirdly, the specific refractive power and heats of combustion of equivalent weights of isomeric alcohols, aldehydes, and other classes of the fatty series are approximately equal. Fourthly, the double binding of carbon-compounds increases the refractive power and heat of combustion, and these constants are greater for those compounds which contain double bindings, than for their isomerides which do not contain such double bindings, whether of carbon with oxygen or of carbon with itself in ring-formed groupings. From this, it may be concluded with probability that the double binding of oxygen increases in like manner the heat of combustion and the refractive power.

Part II. From the determinations of heats of combustion, it follows from thermodynamical considerations that the energy of a compound containing a double bond is greater than the energy of an isomeride which has no such bond. But the energy of a compound consists of the kinetic energy of its particles (its specific heat capacity) and its potential energy, of which the former, in the case of isomeric compounds containing the same number and kind of atoms, is the same for any given temperature. Then the different values of the energy of isomeric compounds, as shown by their different heats of combustion, are due to differences of potential energy, so that weaker atom-affinities correspond to greater potential energy. As compounds containing a double bond have a greater energy, this double bond represents, not as hitherto supposed, a stronger, but a weaker attraction between the atoms linked by it. This conclusion is further confirmed by the researches of Kopp and Buff, by which it has been demonstrated that the specific volume of oxygen, sulphur, and nitrogen is increased when they are combined with carbon by a multiple bond, so that the space occupied by two atoms combined together by a multiple bond is greater than the space occupied by these atoms when combined only by a single bond. Thus the former are further removed from one another than the latter. It has also been shown by

Kekulé that on the oxidation of compounds containing a double bond the splitting up of the molecule takes place always at this bond, and this fact must be dependent upon a weaker attraction between the atoms so linked together. Further, the aldehydes and ketones which contain the grouping  $\text{C}:\text{O}$  easily combine with other elements or radicles, which is not the case with the ethers which contain the grouping  $\text{C.O.C}:$ . This weaker atom-attraction of the so-called double bond, the author proposes to represent graphically, thus:—



and the constitution of benzene by the formula—



Inasmuch as Berthelot has found that the heat of combustion of ethylene oxide is greater than that of acetaldehyde, its isomeride, a result which is in direct contradiction to those mentioned above, the author considers it probable that ethylene oxide (and its homologues) has not the constitution  $\text{CH}_2\text{—O—CH}_2$ , but rather  $\text{CH}_2\text{—O}$ , and



this formula is supported by the fact that ethylene oxide is readily polymerised and combines easily with other compounds.

The author, in conclusion, proposes the terms “single or double unsaturated” instead of “double or triple bond.” V. H. V.

**Pocket Pile with Jointed Elements.** By PULVERMACHER (*Compt. rend.*, **93**, 1020—1021).—The negative elements are hollow cylinders of gilded copper, provided with horizontal arms, by means of which they are hung together, and separated by rings of some insulating material. The latter fit one into another when the chain is rolled up, thus forming a firm compact block. The positive elements consist of spirals of zinc wire connected with a split strip of tinned iron, and insulated from the copper plates by cotton or asbestos. That part of the copper cylinder which acts as the negative element may with advantage be replaced by carbon. In this case the zincs are amalgamated, and the pile dips into a solution of chromic acid contained in a water-tight box. The connections can be made in such a manner as to set in action any wished for number of elements.

C. H. B.

**Thermic Laws Relating to the Exciting Spark in Condensers.** By E. VILLARI (*Compt. rend.*, **92**, 1449—1452).—The “exciting spark” of the discharge of a condenser is to be understood as that which is produced against the exciter, and the “conjunctive spark” as that which is formed in an interruption. In order to measure the heat of the former, a special thermometer was devised, consisting of an exciter enclosed in a glass flask. This flask was

supported by two bands of ebonite passing through two tubulures, in such a manner as to be able to turn round upon its axis horizontally, whereby the circuit of a Leyden jar battery could be opened or closed at pleasure; the spark then passed between two terminals inside the flask.

The heat developed was measured by the displacement of a glycerol and water index contained in a vertical glass tube attached to the flask. With this apparatus, it was found as a mean result, for differing known charges of the same battery—

“That the heat developed by the exciting spark is very nearly proportional to the square of the charge.”

This law is unfortunately complicated by several phenomena, amongst which may be mentioned, the quality of the glass of which the jars were made; its power of retaining an electric discharge; and the production of secondary discharges when working at high potential; however, by using every possible precaution, it was further ascertained that—

(1.) The heat of the exciting spark increases more rapidly than the third power of the charge for a low potential.

(2.) It increases almost directly as the charge for a very high potential.

(3.) It increases as the square of the charge for a mean potential.

The author has also studied the manner in which the heat produced by the spark varies with the quantity of electricity, when the potential remains constant; under these circumstances it was found that the heat increases rather more slowly than the charge, or more exactly, when the charge increases from 1 to 2, the heat produced by the spark augments in the ratio of 1 to 1.77.

When the potential varies and the charge remains constant, the heat increases (1) more rapidly than the potential when the latter is small; (2), directly as the potential of mean value; but (3), it increases much less or even decreases with an increasing potential when the latter is high. In the first case, with a small potential increasing from 1 to 2, the heat of the spark increased in the ratio of 1 to 3.81.

In experiments of this nature, a part of the spark may be replaced by a fine metallic wire, and *vice versa*; but it is necessary that the sum total of all the other effects produced by the spark should follow the same laws. An essential difference exists, nevertheless, between the spark and a heated wire, as far as thermal phenomena go. The spark, according as the charge and potential increase, augments in length and in transverse section; it must, therefore, be regarded as a variable conductor in which the heat is doubtless a function of the number of gaseous molecules which compose it as well as of their temperature. In the case of a metallic wire which is obviously a fixed or invariable conductor, its thermic quality is exclusively a function of temperature.

J. W.

**Disintegration of Electrodes by Positive Electricity, and the Explanation of Lichtenberg Figures.** By E. REITLINGER and F. WÄCHTER (*Ann. Phys. Chem.* [2], **14**, 591—610).—The electrical disintegration which occurs at the surfaces of flat, spherical, or pointed

metallic electrodes, is caused solely by the discharge of positive electricity.

Whenever negative electricity runs over a resinous surface, it always leaves behind it traces of a circular spreading, whilst positive electricity can, according to circumstances, happen either in radial lines, or in circular discs or rings. An inversion of Lichtenberg's figures, by means of which negative electricity would give a radiating figure, is found to be impossible down to the smallest lines or rays.

The positive Lichtenberg radiating figures are caused by minute particles detached from the electrode, whilst the positive as well as the negative disciform figures are produced by gaseous discharges.

T. C.

**New Method of Measuring certain Chemical Affinities.** By A. TRIBE (*Phil. Mag.* [5], 12, 299—300).—The author immerses a rectangular metallic plate in an electrolyte in the act of electrolysis, so that the lines of force are parallel with one of its edges, and from the form and size of the intermedial space (*i.e.*, the space on which neither of the ions is deposited) hopes to be able to measure chemical affinities quantitatively.

F. L. T.

**Specific Heats of Gases at High Temperatures.** By MALLARD and LE CHATELIER (*Compt. rend.*, 93, 1014—1016).—By means of an apparatus previously described, the authors have determined the specific heats at constant volume of carbonic anhydride, water vapour, nitrogen, hydrogen, oxygen, and carbonic oxide, at temperatures near 2000°. The gas experimented with was mixed with a certain proportion of an explosive mixture of oxygen and carbonic oxide, or oxygen and hydrogen, as the case might be, and the pressure developed by the explosion was determined. From this, the temperature was calculated, a correction being made for cooling, and from the temperature the specific heat was readily deduced.

*Carbonic anhydride* ( $\text{CO}_2 = 44$ ), specific heat at about 1800° = 12.6. The determinations of Regnault and of Wüllner give 6.3 as the specific heat at 0°, with an increase of 0.055 for 1°. The author's value corresponds with an increase of 0.038 for 1°. The specific heat of  $\text{CO}_2$  increases continually up to 2000°, but the rate of increase diminishes as the temperature rises. The specific heat at temperature  $t$  may be represented by the formula

$$C = 6.3 + 0.00564t - 0.00000108t^2,$$

which gives a maximum of 13.7 at 2160°. Probably this formula holds good only for temperatures below 2000°, and above this point the specific heat tends to become constant, with a limit of about 13.7.

*Water vapour* ( $\text{H}_2\text{O} = 18$ ), specific heat at 1600° = 11.5. Regnault and Winkelmann found 5.91 at 0°, with an increase of 0.0375 for 1°. The mean specific heat at constant volume between 0° and  $t$  is given by the formula

$$C = 5.91 + 0.00376t - 0.000000155t^2.$$

*Oxygen, Hydrogen, Nitrogen, Carbonic Oxide.*—It is well known that



the specific heats of these gases at  $0^\circ$  are equal. The authors find that they are also equal at temperatures above  $2000^\circ$ . The mean specific heat between  $0^\circ$  and  $t$  is given by the formula

$$C = 5 + 0.00062t^2.$$

The increase in specific heat at  $2000^\circ$  is 2.5.

The authors have proved that none of the gases experimented with undergo dissociation at the high temperature employed.

C. H. B.

**Liquefaction and Cold Produced by the Mutual Action of Solids.** By EVELYN M. WALTON (*Phil. Mag.* [5], 12, 290—298).—The mixing of two dry finely powdered salts, one or both containing water of crystallisation, may be attended by liquefaction to a greater or less extent, with accompanying decrease of temperature, as noticed by Ordway (*Silliman's Journ.* [2], 9, 30; and 27, 15), Berthelot, and Ditte.

As a rule, one solid must be hydrated, but neither need be a salt. When any change, such as double decomposition, oxidation, or reduction can take place, liquefaction is probable. When  $\text{SnCl}_2 + 2\text{H}_2\text{O}$  is mixed with  $\text{HgCl}_2$ ,  $\text{Fe}_2\text{Cl}_6 + 12\text{H}_2\text{O}$ , or  $\text{CuCl}_2 + 2\text{H}_2\text{O}$ , liquefaction occurs, but not if it is mixed with  $\text{PbCl}_2$ .

Moistening occurs on grinding  $\text{AgNO}_3$  and  $\text{HgCl}_2$  together, from which the author suspects the formation of anhydrous mercury nitrate liquid at ordinary temperatures.

When liquefaction occurs with double decomposition, water is usually liberated, *e.g.*,  $\text{Fe}_2(\text{NO}_3)_6, 18\text{H}_2\text{O} + 3[\text{CaCl}_2, 6\text{H}_2\text{O}] = \text{Fe}_2\text{Cl}_6, 12\text{H}_2\text{O} + 3[\text{Ca}(\text{NO}_3)_2, 4\text{H}_2\text{O}] + 12\text{H}_2\text{O}$ , but liquefaction also occurs on mixing two salts of the same base or the same acid, *e.g.*—

$\text{Fe}_2\text{Cl}_6, 6\text{H}_2\text{O}$ with $\text{Fe}_2(\text{NO}_3)_6, 18\text{H}_2\text{O}$ liquefied.		
$\text{Fe}_2\text{Cl}_6, 12\text{H}_2\text{O}$	"	"
$\text{FeCl}_2, 4\text{H}_2\text{O}$	"	"
$\text{FeSO}_4, 7\text{H}_2\text{O}$	"	"
"	with $\text{Fe}_2\text{Cl}_6, 6\text{H}_2\text{O}$	"
$\text{Na}_2\text{C}_2\text{H}_2\text{O}_2, 6\text{H}_2\text{O}$	"	$\text{PbC}_2\text{H}_2\text{O}_2, 3\text{H}_2\text{O}$ "
"	"	$\text{K}_2\text{C}_2\text{H}_2\text{O}_2$ "
"	"	$\text{ZnC}_2\text{H}_2\text{O}_2, 3\text{H}_2\text{O}$ "
$\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$	"	$\text{ZnSO}_4, 7\text{H}_2\text{O}$ "
"	"	$\text{Li}_2\text{SO}_4, \text{H}_2\text{O}$ "
$\text{CaCl}_2, 6\text{H}_2\text{O}$	"	$\text{Fe}_2\text{Cl}_6, 12\text{H}_2\text{O}$ "
"	"	$\text{CuCl}_2, 2\text{H}_2\text{O}$ "

When  $\text{NaOH}$  was used with any hydrated sodium salt, it appropriated the combined water.

The author considers that the liquefaction which takes place on mixing  $\text{CaCl}_2, 6\text{H}_2\text{O}$  with  $\text{Ca}(\text{NO}_3)_2, 4\text{H}_2\text{O}$ , and in similar cases, is because the crystallising point of these two bodies together is lower than for either when alone, just as in the case of ice and common salt. The lowest attainable temperature of sodium nitrate with ice is  $-17^\circ$ . The author, by acting on ice with mixtures of metallic nitrates and sodium

carbonate or sulphate (whereby sodium nitrate and an insoluble carbonate or sulphate would be produced) obtained temperatures varying from  $-13.7^{\circ}$  to  $-26^{\circ}$ , averaging  $-17.7^{\circ}$ . F. L. T.

*Note by Abstractor.*—I can confirm the fact that moistening occurs on rubbing  $\text{AgNO}_3$  and  $\text{HgCl}_2$  together in a mortar, but I find that no moistening and no *increase in weight* occurs, even at the end of twenty hours, on mixing the finely powdered dried salts with a platinum wire and leaving them in a desiccator, whereas on leaving the same mixture for two or three hours exposed to the ordinary atmosphere, moistening and *increase in weight* occur simultaneously; the reason probably being that the highly deliquescent mercuric nitrate formed at each point of contact of the two salts absorbs moisture from the air. It might also be pointed out that in the above cases of liquefaction of salts containing the same acid or the same base, some of the salts employed, *e.g.*, calcium chloride, ferric chloride, ferric nitrate, are more or less deliquescent.

**Calorimetric Studies.** By W. OSTWALD (*J. pr. Chem.* [2], **25**, 1—19).—In order to study the amount of change occurring between the acids and bases of two salts in the fused state, the author has determined the heat of solution of such mixtures before and after fusion. The results obtained cannot always be applied to this purpose, for in many cases where no interchange can have taken place, the heat of solution has still suffered change. This the author attributes to the formation of double salts. In some of these cases the heat of solution of the fused mixtures undergoes slow alteration until it reverts to that of the mixture before fusion: in a mixture, for instance, of potassium and sodium chlorides, before fusion, the heat of solution is  $-5.97$  cal., immediately after fusion,  $-3.67$  cal.; one hour after fusion,  $-3.8$  cal.; one month after fusion,  $-5.98$  cal.

Taking mixtures of salts to which these objections do not apply, the author shows that the heat of solution after fusion is independent of the order of combination of the acids and bases before fusion: thus with potassium sulphate and barium chloride in molecular proportion, before fusion the heat of solution is  $+0.82$  cal.; after fusion,  $-8.76$  cal.; barium sulphate and potassium chloride, before fusion,  $-9.33$  cal.; after fusion,  $-8.9$ , &c. On comparing the amounts of change calculated from these numbers, it is found that the salt having the greatest heat of formation is formed in largest quantity. A. J. G.

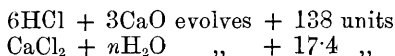
**Affinities of Metals for Oxygen, as shown by the Heat Developed and the Contraction Produced during Combination.** By W. MÜLLER-ERZBACH (*Annalen*, **210**, 196—206).—The results obtained by a study of the chemical reactions of metals have been found to place them in the same order of affinity in the case of their haloid and oxygen salts as their heat of combination and contraction of volume. In the case of the metallic oxides, however, this is different. According to the heat evolved during combination of the hydroxides of the alkaline and alkaline earth-metals, for instance, the order of affinity would be Mg, Sr, Ba, Ca, K, and Na, which by no

means agrees with the results obtained by a study of the chemical reactions of these metals. On the other hand, the contraction of volume on combination follows in the same order as that given by chemical and electrical results. In the case of the monoxides of heavy metals, the heats of combination give the same series as the chemical reactions, whilst the specific gravities of some of the oxides not being known with certainty, the results of contraction of volume cannot be definitely stated. The trioxides,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_3$ , and  $\text{As}_2\text{O}_3$ , seem to follow the same law in heat of combination as in chemical behaviour, and this also holds good when their contraction on combination is studied. Bismuth trioxide alone forms an exception, as according to its sp. gr., the affinity for oxygen of bismuth should be stronger than that of iron, whilst chromium takes its proper place between iron and aluminium.

J. K. C.

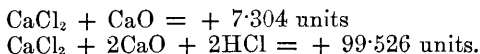
**Heat of Formation of Calcium Oxychloride.** By BERTHELOT (*Compt. rend.*, **92**, 1452—1454).—Crystallised calcium oxychloride was made by boiling together a solution of calcium chloride and slaked lime. Long needle-like crystals were deposited on cooling, which could not be purified by washing either with water or with alcohol, as they were immediately decomposed; they were therefore merely dried by pressure between bibulous paper. An analysis by Ditte assigned to the salt the formula  $\text{CaCl}_2 \cdot 3\text{CaO} \cdot 16\text{H}_2\text{O}$ , which composition has been adopted by the author of the present communication.

The heat of formation of the oxychloride was measured by dissolving it in dilute hydrochloric acid, the reaction being as follows:—

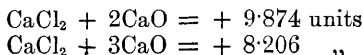


If the heat disengaged during solution, + 31·697 units, be deducted, the heat of combination, starting from solid calcium chloride and calcium oxide, becomes  $\text{CaCl}_2 + 3\text{CaO} + 16\text{H}_2\text{O} = + 92$  units, or 69·12 units, if the water also be reckoned as solid. By drying the oxychloride in a vacuum, it loses 40·9 per cent. of its weight, and these correspond to the formula  $\text{CaCl}_2 \cdot 3\text{CaO} \cdot 3\text{H}_2\text{O}$ . The heat of formation was measured as in the previous instance, and 57·64 units were obtained, reckoning the water as liquid, or 53·37 units with the water as solid.

One molecule of anhydrous calcium chloride was fused with 1, 2, and 3 molecules of quicklime. Their heat of formation is as follows:—

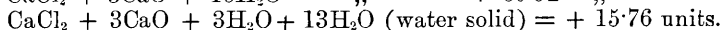
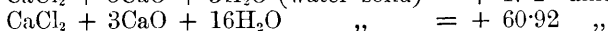
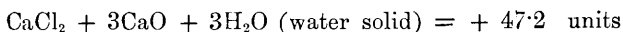


whence—



The numbers expressing the heats of combination of these three compounds approximate very closely to each other, and being within the limits of experimental error, may perhaps be considered as iden-

tical. From them may be calculated the heat evolved by the combination of the anhydrous oxychloride with water.



This last quantity exceeds the heat of hydration of calcium chloride, which explains the formation of the oxychloride in presence of water. J. W.

**Temperatures of Combustion and Dissociation of Carbonic Anhydride and Water Vapour.** By MALLARD and LE CHATELIER (*Compt. rend.*, 93, 1076—1079).—The temperatures of explosive mixtures calculated by means of the formula for specific heats, &c., given in a former paper (this vol., p. 449), agree well with those actually observed. On the basis of these formulæ and determinations, the authors have calculated the temperature of combustion of explosive mixtures of hydrogen with oxygen, and of carbonic oxide with oxygen, and also the temperature of dissociation of water vapour and carbonic anhydride. Assuming that the formula is true for temperatures above  $2700^\circ$ , the temperature of combustion of  $\text{H}_2 + \text{O}$  in a closed vessel is  $3480^\circ$ . The actual temperatures observed with mixtures closely approaching the theoretical mixture in composition varied between  $3100$  and  $3300$ . The dissociation of water is therefore only very slight even at this elevated temperature. Taking into account only the *exterior* work done by the gas in expanding from constant volume to constant pressure, and assuming that the ratio of the two specific heats is the same as at low temperatures, the temperature of combustion of  $\text{H}_2 + \text{O}$  at ordinary pressure is  $3200^\circ$ , supposing that no dissociation takes place. If there is slight dissociation the temperature will be between  $2800^\circ$  and  $2900^\circ$ , a value adopted by Deville. On the same supposition the temperature of combustion of an explosive mixture of hydrogen and air is  $1830^\circ$ .

Assuming that the formula for the variation of the specific heat of carbonic anhydride is true for temperatures above  $2000^\circ$ , the temperature of combustion of  $\text{CO} + \text{O}$  is  $3200^\circ$ , with dissociation to the extent of about 30 per cent. The dissociation of carbonic anhydride is only slight, even at  $2260^\circ$ : this is the temperature of combustion of a mixture of carbonic oxide and air in closed vessels. The temperature of combustion of the same mixture under ordinary conditions, calculated as in the case of hydrogen, is  $2050^\circ$ . C. H. B.

**Explosion of Acetylene, Cyanogen, and Endothermic Compounds in General.** By BERTHELOT (*Compt. rend.*, 93, 613—619).—The author has succeeded in exploding various gaseous compounds by means of special detonating agents. As in the well-known case of dynamite, the violent shock of the exploding charge completely destroys the molecular stability of the gas. The author has generally employed mercury fulminate. He states that there appears to exist an explosive wave quite distinct from proper sound waves.

*Acetylene.*—20—25 c.c. of acetylene were exploded by 0.1 gram of

mercury fulminate. It yielded carbon and free hydrogen. The carbon is deposited in an amorphous state, dissolving almost completely in a mixture of fuming nitric acid and potassium chlorate. There is, however, a trace of graphite, which is probably produced by the exceedingly high temperature. The author has previously shown that amorphous carbon begins to change into graphite when heated to  $2500^{\circ}$  by explosive gas, and also that lamp-black obtained by the incomplete combustion of a hydrocarbon, contains a trace.

*Cyanogen*.—When cyanogen is exploded in a similar manner, it yields amorphous carbon and free nitrogen. There is also a trace of graphite in this case.

*Nitric Oxide*.—On explosion, this gas splits up into nitrogen and oxygen; but the carbonic oxide formed by the decomposition of the mercury fulminate combines with the oxygen, so that the final products are carbonic anhydride and nitrogen.

*Arsenic trihydride* decomposes on explosion into arsenic and hydrogen.

The author states that, generally speaking, compounds and explosive mixtures become more and more susceptible to shocks as they near the temperature at which they begin to decompose. The author states the following general rule: gases formed with absorption of heat, such as those employed in the above experiments, which do not explode by simple heating, can be made to explode by means of a violent shock.

J. I. W.

**Surfaces of Separation.** By BERTHELOT (*Compt. rend.*, **93**, 1054).—The author first stated this principle in 1869 (*Ann. Chem. Phys.*, 140), and not in 1872, as recently stated by Lemoine.

C. H. B.

**Diffusion of Solids into Solids.** By A. COLSON (*Compt. rend.*, **93**, 1074—1076).—When sheet-iron is heated with lamp-black in a reducing atmosphere, not only does the carbon diffuse into the iron, but the iron also diffuses into the carbon. This diffusion will take place at a temperature as low as  $250^{\circ}$  if the heating is prolonged for 24 hours. Piano wire heated to redness with charcoal in a carbon crucible surrounded by a brasque of lamp-black, loses weight, but retains its malleability and metallic lustre: after heating, the carbon contains iron. It would appear that at low temperatures the iron diffuses most readily into the carbon, at high temperatures the reverse is the case. No similar phenomena are observed with platinum. The author concludes that the diffusion of solids is strictly analogous to that of liquids. In order that two solids may diffuse one into the other, it is necessary that there should be some attraction between them, *i.e.*, that they can react upon one another. Silver chloride will diffuse into dry sodium chloride, and metallic silver into dry alkaline chlorides when heated with them at temperatures below their melting points. If a plate of copper is placed on a polished surface of iron pyrites, and heated in a current of carbonic anhydride, small quantities of sulphur are separated from the pyrites and combine with the copper. This experiment may be repeated several times with the same surface of pyrites. When piano wire is heated to redness with pure

lime in a carbon crucible surrounded by a brasque of lamp-black, calcium diffuses into the iron. If the heating is prolonged for three hours, the piano wire becomes brittle. When discs of iron, separated by cylinders of compressed lamp-black, are heated to redness in a cylinder of gas carbon placed in a brasqued crucible, the extent of diffusion follows the law,  $hp = \text{constant}$ , where  $h$  is the distance from the surface of the iron disk and  $p$  the weight of iron in a unit-volume of charcoal at the distance  $h$ .  
C. H. B.

**Incomplete Combustion of Gases.** By K. BÖRSCH (*Annalen*, 210, 207—245).—These experiments were conducted in the apparatus used by V. Meyer. They consisted in the explosion of a mixture of various volumes of carbonic oxide and detonating gas, at diminished pressure, and at various temperatures, and also of the explosion of mixtures of chlorine, oxygen, and hydrogen under varying conditions. The results of the experiments, under diminished pressure, with hydrogen and oxygen in the proportion of two volumes of the former to one of the latter, mixed with varying proportions of carbonic oxide, are given in the table below, where  $p$  and  $t$  represent the pressures and temperatures respectively before the explosion:—

No.	Before explosion.			After explosion.					
	O.	H <sub>2</sub> .	CO.	H <sub>2</sub> O.	CO <sub>2</sub> .	H <sub>2</sub> .	CO.	$p$ .	$t$ .
1....	1	2	2·94	1·32	0·68	0·68	2·26	145	2·9
2....	1	2	1·51	1·35	0·65	0·65	0·86	149	2·3
3....	1	2	0·99	1·44	0·56	0·56	0·43	153	6·6
4....	1	2	0·75	1·67	0·33	0·33	0·41	150	8·1
5....	1	2	0·60	1·74	0·26	0·26	0·34	158	4·9
6....	1	2	0·49	1·77	0·23	0·23	0·26	167	4·5

It will be seen from the above table that the ratio of the carbonic anhydride to the water in the products of combustion is almost constant so long as the carbonic oxide present in the mixture is not less than half the quantity of hydrogen.

Experiments with the same relative quantities of gases were carried on at 100° and 180°, the pressure being also considerably raised. The results are given on the next page:—

No.	At 100°.				<i>p.</i>	<i>t.</i>	At 180°.				<i>p.</i>	<i>t.</i>
	After explosion.						After explosion.					
	H <sub>2</sub> O.	CO <sub>2</sub> .	H <sub>2</sub> .	CO.			H <sub>2</sub> O.	CO <sub>2</sub> .	H <sub>2</sub> .	CO.		
1..	1·18	0·82	0·82	2·13	0·368	98·7	1·11	0·91	0·91	2·1	0·351	180
2..	1·21	0·79	0·79	0·71	0·412	99·0	1·16	0·84	0·84	0·65	0·437	„
3..	1·4	0·6	0·6	0·39	0·488	99·0	1·37	0·63	0·63	0·36	0·387	„
4..	1·53	0·47	0·47	0·27	0·430	99·3	1·49	0·51	0·51	0·24	0·416	„
5..	1·59	0·41	0·41	0·19	0·446	99·1	1·55	0·45	0·45	0·15	0·429	„
6..	1·62	0·37	0·37	0·13	0·421	99·3	1·6	0·4	0·4	0·1	0·448	„

From the above numbers, it will be seen that the amounts of carbonic anhydride and water formed by the explosion increase and decrease respectively with the increase of temperature, and, as was also the case at the ordinary temperature, excess of carbonic oxide has very little influence on the result. In other words, the affinity of carbonic oxide to oxygen increases with the temperature, whilst that of hydrogen to oxygen suffers a relative diminution.

Various mixtures of chlorine, hydrogen, and oxygen were exposed to the action of diffused daylight, the only product being, however, hydrochloric acid. On passing the electric spark through these mixtures, it was found that the chlorine first combined with the hydrogen, and that the formation of water did not commence until the former was saturated; this fact stands in direct contradiction to the theory that the first reaction which takes place between different bodies is that by which the greatest heat is evolved. J. K. C.

### Velocities of Chemical Reactions and Law of Distribution.

By A. POTILITZIN (*Bull. Soc. Chim.* [2], **35**, 667—671).—In a previous communication, (*ibid.*, **35**, 562), the author has shown that complete double decomposition, with disengagement of the theoretical amount of heat, does not take place between any two salts, whether they react in aqueous solution or in absence of water; but that the decomposition stops when it has reached a certain definite limit, and an inverse action then sets in with absorption of heat. The following experiments with the haloïd silver salts have some bearing on this question:—

When freshly precipitated silver bromide is placed in contact with solutions of hydrochloric acid, or of potassium, sodium, lithium, calcium, or barium chloride, the bromide is slowly decomposed, and heat is absorbed; the decomposition is complete only when the chloride is employed in large excess, and when the soluble bromide is continually removed from the solution as it accumulates. In like manner, the displacement of iodine by a soluble bromide is easily effected, but the action of soluble chlorides on silver iodide is slow and imperfect; however, all these reactions are possible, and are accompanied by an

absorption of heat which varies from 3.5 to 6.9 thermal units, when it represents the conversion of silver bromide into chloride, or to 14 units when the change is from iodide to chloride.

As to the inverse actions in which heat is disengaged, they have been studied only in connection with silver chloride and the bromides of potassium and sodium. At first, the displacement of the chlorine is very rapid, but it gradually slackens, so that 165 hours are eventually required to form 95 per cent. of silver bromide by the reaction of potassium bromide, and 96 hours by the action of sodium bromide.

The rapidity of the reaction expressed in amount of decomposition per unit of time, tends consequently towards zero, and the representative curves would, therefore, take the form of equilateral hyperbolas.

In comparing the rapidity of replacement effected by the chlorides of potassium and sodium, it is noticeable that at starting, the double decomposition is greater for sodium chloride than for potassium chloride; this might be anticipated, if the calorimetric effects which accompany the reaction in question are taken into consideration. The transformation of  $\text{AgCl} + \text{KBr}$  into  $\text{AgBr} + \text{KCl}$  in presence of water evolves 3.5 units of heat, whilst the corresponding action of sodium bromide disengages 4.3 units.

The whole of these facts tend to confirm the proposition enunciated by the author in his memoir on "The Measurement of Affinity," that is, the equilibrium of a system of bodies  $\text{AB} + \text{C}$  or  $\text{AB} + \text{CD}$  is not determined by the arrangement corresponding to the maximum amount of heat evolved, but by the distribution of each substance among all the others, according to its respective atomic weight, mass, and temperature.

J. W.

### **Influence of Mass on the Mutual Substitution of Halogens.**

By A. POTILITZIN (*Journ. Russ. Chem. Soc.*, 1882, 82—94).—In several previous papers, the author has studied the action of bromine on metallic chlorides. If equivalent quantities are taken, the quantity of chlorine replaced by bromine is, *cæteris paribus*, proportional to the atomic weights, and inversely proportional to the squares of the atomicity of the respective metals. In the present paper, the author shows that with increasing quantity of bromine the percentage of the chlorine displaced likewise increases; the increments are at first proportional to the square roots of the number of equivalents of the acting bromine, but become smaller and smaller as the quantity of bromine increases, and when a certain limit is reached, an increase in the quantity of bromine, a rise of temperature, or increased heating, has no further action. The experiments were made in vacuous sealed glass tubes, in which a definite quantity of a metallic chloride was heated with weighed but varying quantities of bromine either to 400—450°, or to 310—315°C. Chlorides of Na, K, Ag, Ca, Sr, Ba, Pb, Hg, Bi, were treated in this way with quantities of bromine varying from 1—35 equivalents, and many numerical values were obtained. The higher the temperature, the sooner is the upper limit of displacement reached.



The results of the author's experiments contradict Berthelot's *principe du travail maximum*, because in the above reaction an absorption of heat and *not* a development of heat takes place. The author shows that Berthelot's attempts to bring these reactions into accordance with his principle are unsatisfactory, as, if the difference in the heats of formation of chlorides and bromides has changed its sign at these high temperatures, the displacement of chlorine by bromine ought to be complete, and this is not the case. The same would be the case if polybromides, stable at that high temperature, were formed with a larger development of heat than that of the chlorides. The author shows that on multiplying the differences of the heats of formation of chlorides and bromides of monad elements by the percentage numbers of displacement of chlorine by bromine, a constant value of nearly 4 is obtained. The progress of reactions and their limits depend therefore not alone on the quantity of heat developed (according to the principle of maximum of work), but also upon the atomic weight of the elements, their atomicity, their mass, and the temperature. The author has shown by a direct experiment, that silver chloride in a current of bromine vapour is entirely converted into bromide. Bromine and chlorine displace each other. If they are both present in definite proportions, the mutual displacement reaches a constant limit; if one of them is removed, it will be completely displaced in the compound by the other.

B. B.

**Volume Constitution of Liquid Compounds.** By H. SCHRÖDER (*Ann. Phys. Chem.* [2], **14**, 656—691).—This is a continuation of a previous paper (*ibid.*, **11**, 997) on this subject. The atomic volumes of the elements carbon, hydrogen, and oxygen, when united to carbon by one combining power only, are equal, and are represented by one stere. An atom of oxygen when united to carbon by both affinities, occupies the space of two steres. The  $O_2$  of the carboxyl-group ( $-COOH$ ) of acids corresponds to three steres, because it contains an atom of O in CO with two steres, and an atom of O in the HO-group with one stere. The above rules hold good in the case of all saturated compounds containing carbon, hydrogen, and oxygen, in which all the carbon-atoms are singly linked.

Two carbon-atoms mutually united by two affinities, occupy the space of three steres. In aromatic compounds, the six carbon-atoms of the benzene-ring occupy the space of eight steres, and therefore contain  $C_6^8 = 2 \times C_3^8$ . This fact accords, not with Kekulé's ring structure for benzene, but with Ladenburg's prismatic structure, and hence agrees with the conclusions arrived at by Thomsen from a study of the heats of combustion of aromatic compounds.

T. C.

**Chemical Symmetry, or the Influence of Atomic Arrangement on the Physical Properties of Compounds.** By T. CARNELLEY (*Phil. Mag.* [5], **13**, 112—130; and 180—193).—The influence which atomic arrangement exerts on some of the more important physical properties of isomeric carbon compounds, is traced with the following results:—

(1.) *Melting Point.*—(a.) Of two or more isomeric compounds those

whose atoms are the more symmetrically and the more compactly arranged melt higher than those in which the atomic arrangement is asymmetrical, or in the form of long chains. (b.) Of any number of isomeric compounds, those have the highest melting points in which there are the greater number of side-chains, or in which the main chain of atoms is most branched. These rules were found to hold good in 278 out of the 300 cases (taken at random) to which they were applied. Some of the 22 exceptions may possibly be due to the constitution of the compounds not having been correctly determined, and may thus on closer examination be shown to agree with the rules. These results are merely a first instalment of results which the author hopes to obtain from an exhaustive study of the melting and boiling points of organic compounds, for which object he has collected nearly 30,000 melting and boiling points, about one-half of which are melting points.

(2.) *Solubility.*—Of two isomeric compounds, that dissolves the more easily which has the lower melting point, and in which, therefore, the atomic arrangement is less symmetrical.

(3.) *Heats of Combustion and Formation.*—(a.) The stability, and therefore the heat of formation of symmetrical compounds (and therefore of those with the highest melting points) is greater than that of asymmetrical compounds isomeric with them. b. The heats of combustion of the former compounds are less than those of the latter.

The remainder of the paper deals with the results obtained by van't Hoff (*Bull. Soc. Chim.* [2], **23**, 295), on optical rotation; by Brühl, on molecular refraction; by Liebermann (*Ber.*, **13**, 913), on fluorescence; and by Witt (*Ber.*, **9**, 522) on tinctorial properties, in their dependence on the atomic arrangement.

T. C.

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## Inorganic Chemistry.

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**Occurrence and Formation of Free Fluorine.** By C. LOEW (*Ber.*, **14**, 2441—2442).—In answer to Brauner (*ibid.*, 1944—1946, and this vol., 8) the author maintains that he not only expressed his opinion that the gas in question was free fluorine, but also supplied arguments which made the fact indisputable; and further adds that his explanations were not unfounded. Cerium fluoride is mentioned in Gmelin-Kraut's *Handbuch. d. Chem.*, and there is no reason to suppose that it should not decompose in a manner analogous to the chloride. Only a rise in temperature and not a red heat was used in the experiments, and the vessel, &c., were perfectly dry. He thinks fluorine ought to smell more like chlorine than either bromine or iodine, and of course it does not attack glass. D. A. L.

**Decomposition of Water by the Silent Discharge in Presence of Nitrogen.** By DÉHÉRAIN and MAQUENNE (*Compt. rend.*, **93**, 1021—1023).—The apparatus previously described (*Compt. rend.*, 1881) gives, in presence of liquid water, a discharge with a tension closely approaching that of the spark. It causes the explosion of a mixture

of oxygen and hydrogen almost instantaneously, and under low pressure decomposes water more readily than any other form of apparatus. In presence of nitrogen gas, water is decomposed at ordinary pressures, small quantities of nitric acid being found at the same time. This form of electric discharge brings about the combination of nitrogen gas with organic compounds, such as dextrin and glucose, with production of complex products.

C. H. B.

**So-called Chlorine Trioxide.** By GARZAROLLI-THURNLACKH (*Annalen*, **209**, 184—203).—The gas which is described as chlorine trioxide by Millon (*Ann. Chim. Phys.* [3], **7**, 298); Schiel (*Annalen*, **109**, 317); and Brandau (*Annalen*, **151**, 340), was shown on analysis to be a mixture of free chlorine and chlorine tetroxide,  $\text{Cl}_2\text{O}_4$ .

W. C. W.

**Chlorites.** By GARZAROLLI-THURNLACKH and VON HAYN (*Annalen*, **209**, 203—210).—Although neither chlorine trioxide nor chlorous acid has been prepared, chlorites can be obtained by adding potassium hydroxide to an aqueous solution of chlorine tetroxide,  $\text{Cl}_2\text{O}_4$ , a mixture of potassium chlorate and chlorite being produced. Potassium chlorite crystallises in thin needles. A solution of this salt produces a yellow precipitate with silver and lead solutions. On recrystallisation from hot water, lead and silver chlorites are obtained in yellow plates.

W. C. W.

**Nitrogen Sulphide.** By BERTHELOT and VIEILLE (*Compt. rend.*, **92**, 1307—1309).—Nitrogen sulphide is a well-defined crystalline substance, originally prepared by Fordos and Gélis, by the action of ammonia on sulphur chloride dissolved in carbon disulphide, thus:—



It was analysed by the authors in order to make sure of its composition, after which they proceeded to determine its heat of formation, which, from the physical properties of the substance, it was expected would prove to be negative in sign.

	N	S
Experiment.....	30.41.....	69.64 = 100.05
Theory.....	30.44.....	69.56 = 100.00

The sulphide crystallises well, and is stable in dry and moist air. It can be moistened and dried at  $50^\circ$  several times, without appreciable alteration. It explodes with violence under the hammer; nevertheless its sensibility in this respect is less than that of mercury fulminate or diazobenzene nitrate.

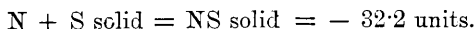
On heating, it deflagrates about  $207^\circ$ , but the deflagration is much slower than with the fulminate. Its density was 2.22 at  $15^\circ$ .

**Heat of Formation.**—The explosion was managed in an atmosphere of nitrogen by means of a fine wire, ignited by a galvanic current in an ordinary calorimetric apparatus. Two experiments were conducted on 2.997 and 2.279 grams of substance. They gave for 1 gram 701 units and 700.4 units respectively.

The corrected volume of the gases produced was for 1 gram 244 c.c.

and 242.2 c.c. = 243 c.c. as a mean, or 11.18 litres for NS, the theoretical volume being 242.1 c.c.

The heat of formation of nitrogen sulphide is therefore negative—



The sign of this heat of formation is the same as for nitrogen oxide, thus:  $\text{N} + \text{O} = \text{NO gas} = -21.6$  units, which is a new proof of the analogy which exists between the heats of formation of oxygen and of sulphur compounds.

The tension developed by explosion in closed vessels was determined.

Weight of charge.	Pressure in kilos. per sq. centimetre.	
	Nitrogen sulphide.	Mercury fulminate.
0.1	815	480
0.2	1703	1703
0.3	2441	2700

The pressures developed by the explosion of nitrogen sulphide are, as may be seen, very similar to those obtained with the fulminate in the two latter experiments. If the explosion detonated in its own volume, the pressure would be double with the fulminate. But the rapidity of the decomposition being very different, the effects produced by the two substances, supposing them to be used as detonators or "fuses," would be very dissimilar.

J. W.

**Spontaneously Inflammable Hydrogen Phosphide.** By J. BRÖSSLER (*Ber.*, 14, 1757—1759).—According to Dumas (*Ann. Chim. Phys.*, 31, 135) this gas is not produced when ordinary phosphorus is added to zinc and sulphuric acid; neither is the inflammable gas evolved at 100° from this mixture anything more than hydrogen carrying with it some phosphorus vapour. The author, on the contrary, finds that an evolution of spontaneously inflammable gas commences at 40° and continues to increase up to 70°; further, that when the evolution has once commenced, it continues even when the temperature of the liquid sinks to 20°. The gas so obtained is absorbed by copper sulphate, and therefore contains hydrogen phosphide. This gas is also produced when phosphorus is added to a mixture of zinc and potash heated to 60°. When phosphorus is added to tin and hydrochloric acid, the ordinary hydrogen phosphide is produced; if a few drops of nitric acid are added, then the spontaneously inflammable phosphide is produced.

P. P. B.

**Hypophosphoric Acid.** Part III. By T. SALZER (*Annalen*, 211, 1—35).—To prepare hypophosphoric acid, sticks of phosphorus placed in glass cylinders are half covered with water. Several of these cylinders are suspended by a string, in an earthenware mug, which is loosely covered with a sheet of glass. Every third day the liquid in the cylinders is collected, and the sticks of phosphorus are again half covered with water. The aqueous solution contains a mixture of phosphorous, orthophosphoric, and hypophosphoric acids. Pure hypophosphoric acid is more easily prepared by the action of dilute sulphuric

ric acid on an excess of barium hypophosphate, than by the decomposition of the lead salt with sulphuretted hydrogen.

At the ordinary temperature, hypophosphoric acid decomposes into phosphorous and pyrophosphoric acids:  $2\text{H}_4\text{P}_2\text{O}_6 + \text{H}_2\text{O} = 2\text{H}_3\text{PO}_3 + \text{H}_4\text{P}_2\text{O}_7$ .

Hypophosphoric acid has the composition  $\text{H}_4\text{P}_2\text{O}_6$ , and forms the following salts: *Tetrapotassium hypophosphate*,  $\text{K}_4\text{P}_2\text{O}_6 + 5\text{H}_2\text{O}$ , prepared by the addition of (2 mols.) potassium hydroxide to dipotassium hypophosphate (1 mol.), crystallises in rhombic pyramids or plates,  $a : b : c = 0.9458 : 1 : 1.0124$ . The salt is soluble in less than one-fourth of its weight of water, forming a strongly alkaline solution which does not, however, absorb carbonic acid from the atmosphere. It is insoluble in alcohol, but is not precipitated from an aqueous solution by the addition of alcohol.

*Tripotassium hypophosphate*,  $\text{K}_3\text{HP}_2\text{O}_6 + 3\text{H}_2\text{O}$ , prepared by the addition of potassium hydroxide (1 mol.) to a solution of dipotassium hypophosphate (1 mol.) crystallises in the monoclinic system,  $a : b : c = 0.4224 : 1 : 0.9902$ .  $\beta = 89^\circ 35'$ . The crystals are soluble in half their weight of water, forming an alkaline solution, but are insoluble in alcohol. They lose their water of crystallisation at  $100^\circ$ , and at a higher temperature burn, forming potassium pyro- and metaphosphate.

*Dipotassium hypophosphate*,  $\text{K}_2\text{H}_2\text{P}_2\text{O}_6$ , obtained by digesting monobarium hypophosphate with a solution of potassium sulphate, forms rhombic crystals containing 3 mols.  $\text{H}_2\text{O}$  [ $a : b : c = 0.9873 : 1 : 0.9190$ ], and also monoclinic plates containing—

2 mols.  $\text{H}_2\text{O}$  [ $a : b : c = 0.7241 : 1 : 0.7949$ ].  $\beta = 81^\circ 50'$ .

Both these salts dissolve in 3 parts of cold and in 1 part of hot water. They are precipitated from the aqueous solution by the addition of alcohol.

*Monopotassium hypophosphate*,  $\text{KH}_3\text{P}_2\text{O}_6$ . This salt deposits monoclinic prisms when a hot concentrated solution of the dipotassium hypophosphate containing hypophosphoric acid is allowed to cool slowly. It is soluble in  $1\frac{1}{2}$  parts of cold, and in  $\frac{1}{2}$  part of hot water. The solutions, which have an acid reaction, give a precipitate with alcohol. On spontaneous evaporation, the cold aqueous solution yields tripotassium dihypophosphate; whilst the hot solution contains, in addition to this salt, the tripotassium hypophosphate. The monohypophosphate undergoes no change at  $100^\circ$ , but at  $120^\circ$  it absorbs moisture from the air, forming phosphorous acid and potassium pyrophosphate.

*Tripotassium dihypophosphate*,  $\text{K}_3\text{H}_5(\text{P}_2\text{O}_6)_2 + 2\text{H}_2\text{O}$ , is deposited when a solution containing 3 mols. dipotassium hypophosphate and 1 mol. hypophosphoric acid is evaporated. If a smaller proportion of acid is used, this salt is also formed, but is apt to contain monopotassium hypophosphate. The pure salt is soluble in 2.5 parts of cold and in 0.8 part of boiling water. On the addition of alcohol to the aqueous solution, dipotassium hypophosphate is precipitated. The crystals become anhydrous at  $100^\circ$ .

*Tetra-, tri-, and di-sodium hypophosphate* have been previously

described by the author (Abstr., 1879, 105). The monosodium salt,  $\text{NaH}_3\text{P}_2\text{O}_6 + 2\text{H}_2\text{O}$ , prepared in the same way as the corresponding potassium salt, crystallises in monoclinic plates—

$$a : b : c = 2.0023 : 1 : 1.0907. \beta = 82^\circ 41'.$$

It cannot be recrystallised without decomposition.

*Pentasodium dihypophosphate*,  $\text{Na}_5\text{H}_3(\text{P}_2\text{O}_6)_2 + 20\text{H}_2\text{O}$ , is formed by boiling 2.7 grams of sodium carbonate with 10 grams of disodium hypophosphate dissolved in 80 c.c. of water. It is deposited from the solution in monoclinic plates [ $a : b : c = 1.3638 : 1 : 0.5762$ .  $\beta = 78^\circ 38'$ ], which are frequently mixed with crystals of the di- and tri-hypophosphate. This salt dissolves in 15 parts of cold water, forming a solution of the di- and mono-salts.

*Diammonium hypophosphate* is soluble in 14 parts of cold water and in 4 of boiling water. It undergoes no change at  $160^\circ$ . It resembles the tripotassium dihypophosphate in crystalline form. Monammonium hypophosphate is freely soluble in water.

*Monobarium hypophosphate* is best prepared by adding a solution of 12 grams of barium chloride in 120 c.c. of water, to 16 grams of disodium hypophosphate dissolved in 1 litre of water, containing 6 c.c. of hydrochloric acid (sp. gr. 1.124). After two days, the precipitate is collected and washed with cold water.

In estimating hypophosphoric acid by means of a standard solution of potassium permanganate, the substance must be dissolved in a small quantity (10 c.c.) of boiling water. The permanganate must be added to the boiling solution immediately after the liquid is acidified with sulphuric acid.

W. C. W.

**Sulphur Oxychlorides.** By J. OGIER (*Compt. rend.*, **94**, 82—86).—The heats of formation of the different oxychlorides were calculated from the heat developed by their decomposition with water or potassium hydroxide. *Sulphuryl chloride*, obtained by the action of chlorine on sulphurous anhydride in presence of charcoal, b. p.  $69.9^\circ$ ,  $\text{S} + \text{O}_2 + \text{Cl}_2 = \text{SO}_2\text{Cl}_2$ , liquid, develops 89.6 cals. Specific heat between  $15^\circ$  and  $63^\circ = 0.233$ ; heat of vaporisation,  $\text{SO}_2\text{Cl}_2 = 7.06$  cals., hence  $\text{S} + \text{O}_2 + \text{Cl}_2 = \text{SO}_2\text{Cl}_2$ , gas, develops + 82.54 cals., and  $\text{SO}_2 + \text{Cl}_2 = \text{SO}_2\text{Cl}_2$ , gas, develops + 13.3 cals. *Thionyl chloride*, prepared by the action of sulphurous anhydride on phosphorus pentachloride, could not be completely freed from phosphoryl chloride by fractionation.  $\text{S} + \text{O} + \text{Cl}_2 = \text{SOCl}_2$ , liquid, develops + 47.2 cals. Specific heat between  $17^\circ$  and  $60^\circ = 0.2435$ ; heat of vaporisation,  $\text{SOCl}_2 = 6.48$  cals., hence  $\text{S} + \text{O} + \text{Cl}_2$ , gas, develops + 40.8 cals. The analogous decomposition of phosphorus pentabromide by sulphurous anhydride would absorb heat: hence thionyl bromide cannot be obtained by this reaction, a fact which the author has verified by experiment. *Pyrosulphuryl chloride*, b. p.  $140.5^\circ$ , was obtained by the action of sulphuric anhydride on sulphur chloride. The action of sulphuric anhydride on chloroform gives the compound  $\text{SO}_3\text{HCl}$ .  $\text{S}_2 + \text{O}_5 + \text{Cl}_2 = \text{S}_2\text{O}_5\text{Cl}_2$ , liquid, develops + 159.4 cals. Specific heat between  $15^\circ$  and  $130^\circ = 0.258$ ; heat of vaporisation,  $\text{S}_2\text{O}_5\text{Cl}_2$  13.16 cals., hence  $\text{S}_2 + \text{O}_5 + \text{Cl}_2 = \text{S}_2\text{O}_5\text{Cl}_2$ , gas, develops + 146.2 cals.

The difference between the heats of formation of sulphuryl and thionyl chloride is much greater than between those of sulphuric and sulphurous anhydrides. The difference between the heats of formation of pyrosulphuryl chloride and sulphuric anhydride ( $2\text{SO}_3$ ) is — 37·4 cals., hence the former cannot be produced, as the author has found, by the direct union of sulphuric anhydride and sulphuryl chloride. Pyrosulphuryl chloride decomposes at about  $250^\circ$  into sulphuric anhydride, chlorine, and sulphurous anhydride.

C. H. B.

### Preparation of Rubidium and Cæsium, and of their Salts.

By C. SETTERBERG (*Annalen*, **211**, 100—116).—In order to extract the cæsium and rubidium from the alums, obtained as a bye-product in the manufacture of lithia from lepidolite, a hot solution of three or four cwt. of the crude alum is prepared, having a density of  $20^\circ$  Beaumé, when hot. The liquid is allowed to cool down slowly to  $45^\circ$ , when the cæsium and rubidium alums are deposited, since they are insoluble in a cold concentrated solution of potash alum. The greater part of the potassium alum remains in solution. The impure rubidium and cæsium alums are dissolved in a small quantity of hot water; the solution, on cooling again, deposits rubidium and cæsium alums, leaving the potassium alum in solution. The recrystallisation is continued until the potash is completely removed. Cæsium alum is insoluble in a saturated solution of rubidium alum, so that these two salts may be separated by a repetition of the above process.

The following table shows the amount of the alums (dried at  $130^\circ$ ) which are dissolved by 100 parts of water. Column 4 shows the relative solubility of the two alums, *i.e.*, the solubility of the rubidium alum divided by the solubility of the cæsium alum.

Cæsium alum. $t^\circ$ .	Rubidium alum.	Cæsium alum.	Rubidium alum. Cæsium alum.
0	0·71	0·19	3·74
10	1·09	0·27	3·76
17	1·42	0·38	3·74
25	1·85	0·49	3·78
35	2·67	0·69	3·87
50	4·98	1·235	4·05
60	9·63	2·38	4·05
80	21·60	5·29	4·08

The rubidium alum crystallises in octohedra, exhibiting small cubical and dodecahedral faces. Cæsium alum is deposited from an aqueous solution in a combination of the octohedron with the cube and pentagonal dodecahedron. In the crystals deposited from a hydrochloric acid solution, the pentagonal dodecahedron preponderates.

The best method of preparing the various salts from the alums is to precipitate the alumina from a hot solution by baryta-water, in preference to ammonia. Cæsium or rubidium sulphate remains in solution, and from the sulphate the other salts can be prepared by double decomposition.

Although metallic rubidium can easily be prepared by heating a



mixture of sugar, charcoal, charred acid rubidium tartrate and chalk, caesium could not be obtained by this method. Attempts to prepare caesium by the electrolysis of the chloride were also unsuccessful, a subchloride apparently being formed. The electrolysis of the cyanide yields satisfactory results. Caesium cyanide is prepared by passing anhydrous hydrocyanic acid into a solution of caesium hydroxide in absolute alcohol. Aqueous hydrocyanic acid cannot be used, as the cyanide decomposes during the process of drying. To prepare the metal, a mixture of barium cyanide (1 part) and caesium cyanide (4 parts) is heated to the melting point in a porcelain crucible, and an electric current passed through the molten mass. (Aluminium poles must be used, as other metals and even graphite are rapidly destroyed.) The contents of the crucible are warmed under petroleum, when the metal melts and collects together in globules.

Metallic caesium resembles potassium and rubidium in appearance. It is silver-white, and soft at the ordinary temperature. It oxidises quickly in the air, and takes fire when thrown on water.

The metal melts between 26° and 27°. Its sp. gr. is 1.88 at 15° C.

W. C. W.

**Composition of Sodium Hyposulphite (Schützenberger's Hydrosulphite).** By A. BERNTHSEN (*Annalen*, **211**, 285—305).—In this paper the author gives numerous analytical determinations confirmatory of the formula  $\text{Na}_2\text{S}_2\text{O}_4$ , which he had previously assigned to the salt obtained, together with other products, by the action of zinc on a solution of hydrogen-sodium sulphite (regarded by Schützenberger, who discovered it, as having the composition  $\text{Na}_2\text{SO}_3$ ; cf. *Abstr.*, 1881, 508, 682, 978). The action of zinc on a solution of hydrogen-sodium sulphite may be represented by the equation—



the oxidation of hyposulphurous acid by iodine, by the equation  $\text{H}_2\text{S}_2\text{O}_4 + 3\text{I}_2 + 4\text{H}_2\text{O} = 2\text{H}_2\text{SO}_4 + 6\text{HI}$ ; and its oxidation by cupric sulphate, by the equation  $\text{H}_2\text{S}_2\text{O}_4 + \text{O} + \text{H}_2\text{O} = 2\text{H}_2\text{SO}_3$ .

H. W.

**Solubility of Barium and Strontium Sulphates in Concentrated Sulphuric Acid.** By E. VARENNE and PAULEAU (*Compt. rend.*, **93**, 1016—1017).—The solubility of barium sulphate was determined by adding sulphuric acid of 91 per cent. to a known volume of a solution of the chloride or nitrate, containing respectively 5.0235 and 5.175 gram of salt per litre, until the precipitate was just redissolved, or by adding the saline solution to a known volume of the acid until a permanent turbidity was produced. 1 gram of barium sulphate precipitated from the nitrate dissolves in 1519 grams of sulphuric acid of 91 per cent.; 1 gram precipitated from the chloride requires 3153 grams of acid for complete solution. The difference is probably due to the action of the nitric acid liberated. 1 gram strontium sulphate precipitated from the chloride dissolves in 1256 grams of the sulphuric acid. In all cases, the coefficients of solubility are independent of the masses of the solutions employed. The coefficients of solubility of strontium and barium sulphates are sensibly proportional to their equivalents.

C. H. B.

**Combination of Lead Iodide with Alkaline Iodides.** By A. DITTE (*Compt. rend.*, 92, 1341—1344).—When lead iodide is put into a solution of potassium iodide, it dissolves at first slowly, afterwards more rapidly, until the solution is saturated; after a time, the liquid becomes filled with white needles which have only the slightest yellow tinge. These crystals have the composition  $\text{PbI}_2 \cdot 2\text{KI} \cdot 4\text{H}_2\text{O}$ ; they are decomposed, with re-formation of lead iodide, both by addition of water, and by raising the temperature of the solution; alcohol produces the same effect.

The study of this decomposition was effected (1) by adding water to a great excess of the double iodide, so as to decompose only a part, and analysing the liquor, when the action was complete; (2) by adding potassium iodide by degrees to a mixture of water and lead iodide until needles of the double salt begin to form, and then analysing the liquid in contact with the double iodide. In this way it was possible to ascertain the weight of alkaline iodide which at any given temperature is necessarily present, so as to prevent decomposition of the double salt. These quantities are, per litre of liquid, at 5°, 140 grams; at 10°, 160 grams; at 20°, 204 grams; at 39°, 300 grams; at 59°, 503 grams; at 85°, 738 grams of potassium iodide.

Thus the decomposition of the double iodide of lead and potassium follows the general law, namely, that at all temperatures a liquid, in which the double salt is capable of existing without being decomposed, must contain a definite and minimum quantity of alkaline iodide. No reaction takes place when water, lead iodide, and potassium iodide are brought together; if the proportion of the latter is less than that already indicated, a very little lead iodide only dissolves; if the alkaline iodide is in sufficient quantity, the two iodides will combine until there remains in the liquor just sufficient alkaline iodide to prevent the decomposition of the double salt. The same phenomena take place if sodium or ammonium iodide is substituted for potassium iodide.

J. W.

**Molecular Weight of Mercurous Chloride.** By M. FILETI (*Gazzetta*, 1881, 341—346).—The vapour-density of this compound was first determined in 1833 by Mitscherlich, who obtained the number 8·31 (air = 1), and afterwards, by Deville and Troost, in 1857, who found it to be 8·21. According to these numbers, the molecular formula of calomel should be  $\text{HgCl}$  [ $\text{Hg} = 200$ ]. Odling, however, in 1864, showed that gold-leaf immersed in calomel-vapour, becomes amalgamated, and at the same time covered with a deposit of mercuric chloride; whence he inferred that the mercurous chloride, at the temperature required for the determination of its vapour-density, is resolved into mercuric chloride and metallic mercury, each occupying 2 volumes, so that the entire vapour occupies 4 volumes, and the density 8·31, corresponds with the molecular formula  $\text{Hg}_2\text{Cl}_2$ , which is, moreover, in accordance with the law of even numbers. About the same time, Erlenmeyer observed that when calomel was strongly heated for half an hour in a glass flask, and a tube containing mercury was immersed in the vapour, the mercury began to boil, and after the whole had cooled, the inner surface of the flask and that of the tube just above the level of the liquid were found to be covered with

globules of mercury, mixed with calomel and corrosive sublimate. Hence Erlenmeyer inferred that dissociation had taken place, remarking, however, that the result was by no means decisive as to the vapour-density of calomel, inasmuch as the resolution of that compound into  $\text{HgCl}_2$  and  $\text{Hg}$  may be explained equally well, whether we suppose it to be represented by the formula  $\text{HgCl}$  or by  $\text{Hg}_2\text{Cl}_2$ .

Debray, in 1868, found, on the other hand, that gold-leaf immersed in vapour of calomel at  $440^\circ$  (about the temperature at which the vapour-density would be determined) showed no signs of amalgamation, and thence concluded that the compound had not undergone dissociation. Lebel, however, pointed out that at the temperature in question amalgamated gold parts with all the mercury that it has taken up, and therefore concluded that Debray's observation by no means disproves the view advanced by Odling.

In 1876, Debray, by heating calomel to  $440^\circ$  in a platinum tube within which was a U-shaped tube of gilt-silver traversed by a stream of water, found that the layer of gold became amalgamated, and thence inferred that dissociation really takes place; but he further observed that the deposit thus formed consisted in great part of condensed calomel, and thence inferred that the dissociation was only partial. The same conclusion has been arrived at by Marignac (1868), by measuring the latent heat of volatilisation of calomel; he concludes, indeed, that the amount of dissociation is *extremely limited*, whence it would follow that calomel cannot have the formula  $\text{Hg}_2\text{Cl}_2$ , which requires a vapour-density 16.28 instead of 8.14, whereas if we admit the formula  $\text{HgCl}$ , the vapour-density should be 8.14, whether the dissociation be partial or total.

To throw further light on this question, the author of the present paper has examined the effect of heating a mixture of calomel and mercuric chloride to a temperature of about  $400^\circ$  in an apparatus similar to that of Debray's above described. Under these circumstances he found that no dissociation of the calomel took place, the gilded tube not exhibiting the slightest trace of amalgamation. This being established, he proceeded to determine the vapour-density of a mixture of mercurous and mercuric chloride by V. and C. Meyer's method. One experiment made in this way gave for mercurous chloride the value 8.01; another 8.30, whence it follows that the molecular formula of mercurous chloride is  $\text{HgCl}$ . For the vapour-density of cuprous chloride V. and C. Meyer (*Ber.*, 12, 1116) found numbers leading to the double molecular formula  $\text{Cu}_2\text{Cl}_2$ . H. W.

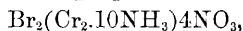
**Electrolysis of Solutions of Antimony Chloride; Explosive Antimony.** By F. PFEIFER (*Annalen*, 209, 161—184).—The ratio between the weights of metallic silver and metallic antimony deposited by the same galvanic current is independent of the strength of the current or of the solutions. It is also independent of temperature.

Explosive antimony, discovered by Gore (this Journal, N.S., 1, 365), is a compact amorphous body containing from 4.8 to 7.9 per cent. of antimony chloride. It also contains small quantities of hydrochloric acid and water, but no occluded hydrogen. Pure crystalline metallic antimony is deposited when a galvanic current is passed through a

solution which does not contain more than 7 per cent. of antimony chloride. The sp. gr. of the explosive antimony diminishes as the amount of antimony chloride contained in it increases.

W. C. W.

**Contributions to the Chemistry of the Chromammonium Compounds.** By S. M. JÖRGENSEN (*J. pr. Chem.* [2], 25, 83—95).—For the first part of this paper see Abstr., 1880, 10. II. *Bromopurpureochromium Salts*.—*Bromopurpureochromium bromide* is prepared by boiling roseochromium hydroxide with excess of concentrated hydrobromic acid, or by heating roseochromium bromide at 100°, when it loses water of crystallisation and is transformed into the bromopurpureochromium bromide. It forms a violet-red crystalline powder, resembling chloropurpureocobalt chloride in colour, but is more sparingly soluble in water, and yields a more violet-coloured solution than the chlorochloride. On gently heating its solution, it is readily transformed into the roseobromide. In general its behaviour with reagents closely resembles that of the chlorochloride. *Bromopurpureochromium chloride*,  $\text{Br}_2[\text{Cr}_2.10\text{NH}_3].\text{Cl}_4$ , is prepared by pouring a solution of the bromobromide into excess of hydrochloric acid diluted with an equal volume of water. It forms a violet-red precipitate consisting of microscopic octohedra. *Bromopurpureochromium nitrate*,



is prepared in like manner, and resembles the above. On treating its cold aqueous solution with normal potassium chromate, a reddish-brown granular precipitate of *bromopurpureochromium chromate*,  $\text{Br}_2(\text{Cr}_2.10\text{NH}_3)_2\text{CrO}_4$ , is obtained: under the microscope it is seen to consist of rhombic tables.

III. *Iodopurpureochromium Salts*.—On boiling roseochromium iodide with concentrated hydriodic acid, a violet crystalline powder of *iodopurpureochromium iodide*,  $\text{I}_2(\text{Cr}_2.10\text{NH}_3)_4$ , is obtained. It can also be prepared by heating rhodochromium iodide with concentrated hydriodic acid, but is best obtained by heating roseochromium iodide at 110°. It forms a bluish-violet crystalline powder, sparingly soluble in water. The iodopurpureochromium chloride, bromide, nitrate, and platinochloride were prepared, and resembled the corresponding chloro- and bromo-compounds.

A. J. G.

**Sodium Ammonium Trimolybdate.** By F. MAURO (*Ber.*, 14, 1379—1382).—This salt is prepared by boiling a solution of borax with an equal weight of ammonium molybdate,  $3(\text{NH}_4)_2\text{O}, 7\text{MoO}_3, 4\text{H}_2\text{O}$ , and separates immediately as a copious white bulky curdy precipitate, slightly soluble in cold, more soluble in hot water, and separating from the solution after some days in its original state. Under the microscope, it is seen to consist of very delicate needle-shaped transparent crystals. When dried between filter-paper and heated to about 110°, it suffers no apparent loss of weight, but merely blackens a little. After fusion and recrystallisation, it acquires a crystalline aspect, and a fibrous structure, or the form of small needles having a lustre like that of molybdic anhydride. Its analysis led to the formula  $(\text{NH}_4)_2\text{O}, \text{Na}_2\text{O}, 6\text{MoO}_3, 2\text{H}_2\text{O}$  or  $(\text{NH}_4, \text{Na})\text{O}, 3\text{MoO}_3, \text{H}_2\text{O}$ . It is a de-

composition-product of another new compound, which crystallises well, and is decomposed by water, but has not yet been obtained in the state of purity required for analysis. H. W.

**Colloidal Tungstic Acid and its Analogy with Paratungstic Acid.** By D. KLEIN (*Bull. Soc. Chim.* [2], **36**, 643).—Colloidal tungstic acid dried at  $200^{\circ}$  has the composition  $12\text{WO}_3 \cdot 4\text{H}_2\text{O}$  (Graham). One of the molecules of water of constitution of the silico-duodecitungstates and the borotungstates, complex derivatives of the paratungstates, appears to be held in combination more loosely than the others. Dipotassium silico-duodecitungstate, for example, loses 1 mol.  $\text{H}_2\text{O}$  above  $150^{\circ}$  (Marignac). Probably if paratungstic acid,  $12\text{WO}_3 \cdot 5\text{H}_2\text{O}$ , could be isolated, it would be found to lose 1 mol.  $\text{H}_2\text{O}$  more readily than the others, giving an acid identical in composition with colloidal tungstic acid dried at  $200^{\circ}$ . C. H. B.

**Phosphotungstates.** By WOLCOTT GIBBS (*Am. Chem. J.*, **2**, 217—234 and 281—294).—The author has continued his experiments on these salts already reported in this Journal (1877, **2**, 247), and has arrived at the following general results:—

1. The phosphotungstates form a series, of which the lowest term probably contains 6 mols. tungstic to 1 mol. phosphoric oxide, and the highest 24 mols. tungstic to 1 mol. phosphoric oxide.

2. At least the greater number of phosphotungstates contain an even number of molecules of tungstic oxide. The homologising term for these cases is therefore  $2\text{WO}_3$ .

3. The highest number of molecules of base observed in any case is six (old style), which implies that the acid contains twelve hydroxyl-groups.

4. In all cases the number of hydroxyl-groups replaced by a monatomic metal is even.

5. In all the phosphotungstates studied, the number of molecules of base, or the number of hydroxyl-groups, is more than sufficient to saturate the phosphoric oxide present, if we suppose that the acid is 12-basic. A part at least of the hydroxyl or base must therefore be united to tungstic oxide.

The following table exhibits the composition of the phospho- and arsenio-tungstates prepared and analysed by the author. In the formulæ in the right-hand column, all the acids are regarded as 12-basic.

$24\text{WO}_3, \text{P}_2\text{O}_5, 6\text{H}_2\text{O} + 47\text{aq.}$	or $\text{W}_{24}\text{P}_2\text{O}_{71}(\text{HO})_{12} + 47\text{aq.};$ also with 34 and 55aq.
$24\text{WO}_3, \text{P}_2\text{O}_5, 2\text{Na}_2\text{O}, 4\text{H}_2\text{O} + 23\text{aq.}$	„ $\text{W}_{24}\text{P}_2\text{O}_{71}(\text{NaO})_4(\text{HO})_8 + 23\text{aq.}$
$24\text{WO}_3, \text{P}_2\text{O}_5, 3\text{K}_2\text{O}, 3\text{H}_2\text{O} + 8\text{aq.}$	„ $\text{W}_{24}\text{P}_2\text{O}_{71}(\text{KO})_6(\text{HO})_6 + 8\text{aq.}$ also with 14aq.
$24\text{WO}_3, \text{P}_2\text{O}_5, 3(\text{NH}_4)_2\text{O}, 3\text{H}_2\text{O} + 16\text{aq.}$	„ $\text{W}_{24}\text{P}_2\text{O}_{71}(\text{NH}_4\text{O})_6(\text{HO})_6 + 26\text{aq.}$
$24\text{WO}_3, \text{P}_2\text{O}_5, 3\text{BaO}, 3\text{H}_2\text{O} + 43\text{aq.}$	„ $\text{W}_{24}\text{P}_2\text{O}_{71}(\text{BaO}_2)_3(\text{HO})_6 + 43\text{aq.}$
$22\text{WO}_3, \text{P}_2\text{O}_5, 2\text{K}_2\text{O}, 4\text{H}_2\text{O} + 2\text{aq.}$	„ $\text{W}_{22}\text{P}_2\text{O}_{65}(\text{KO})_4(\text{HO})_8 + 2\text{aq.}$
$22\text{WO}_3, \text{P}_2\text{O}_5, 3(\text{NH}_4)_2\text{O}, 3\text{H}_2\text{O} + 18\text{aq.}$	„ $\text{W}_{22}\text{P}_2\text{O}_{65}(\text{NH}_4\text{O})_6(\text{HO})_6 + 18\text{aq.}$

$22\text{WO}_3, \text{P}_2\text{O}_5, 2\text{Na}_2\text{O}, 4\text{H}_2\text{O} + 5\text{aq.}$	or $\text{W}_{22}\text{P}_2\text{O}_{65}(\text{NaO})_4(\text{HO})_8 + 5\text{aq.}$
$22\text{WO}_3, \text{P}_2\text{O}_5, 4\text{BaO}, 2\text{H}_2\text{O} + 39\text{aq.}$	„ $\text{W}_{22}\text{P}_2\text{O}_{65}(\text{BaO}_2)_4(\text{HO})_4 + 39\text{aq.}$
$20\text{WO}_3, \text{P}_2\text{O}_5, 6\text{BaO} + 48\text{aq.}$	„ $\text{W}_{20}\text{P}_2\text{O}_{59}(\text{BaO}_2)_6 + 48\text{aq.}$
$18\text{WO}_3, \text{P}_2\text{O}_5, 6\text{K}_2\text{O} + 23\text{aq.}$	„ $\text{W}_{18}\text{P}_2\text{O}_{53}(\text{KO})_{12} + 23 \text{ and } 30\text{aq.}$
$18\text{WO}_3, \text{P}_2\text{O}_5, \text{K}_2\text{O}, 5\text{H}_2\text{O} + 14\text{aq.}$	„ $\text{W}_{18}\text{P}_2\text{O}_{53}(\text{KO})_2(\text{HO})_{10} + 14\text{aq.}$
$16\text{WO}_3, \text{P}_2\text{O}_5, \text{CaO}, 5\text{H}_2\text{O} + 3\text{aq.}$	„ $\text{W}_{16}\text{P}_2\text{O}_{47}(\text{CaO})_2(\text{HO})_{10} + 3\text{aq.}$
$16\text{WO}_3, \text{P}_2\text{O}_5, 4\text{K}_2\text{O}, 2\text{H}_2\text{O} + 19\text{aq.}$	„ $\text{W}_{16}\text{P}_2\text{O}_{47}(\text{KO})_8(\text{HO})_4 + 19\text{aq.}$
$16\text{WO}_3, \text{P}_2\text{O}_5, 6(\text{NH}_4)_2\text{O} + 10\text{aq.}$	„ $\text{W}_{16}\text{P}_2\text{O}_{47}(\text{NH}_4\text{O})_{12} + 10\text{aq.}$
$14\text{WO}_3, 2\text{P}_2\text{O}_5, 5\text{Na}_2\text{O} + 42\text{aq.}$	
$6\text{WO}_3, \text{As}_2\text{O}_5, 3\text{K}_2\text{O}, 3\text{H}_2\text{O}$	„ $\text{W}_6\text{As}_2\text{O}_{27}(\text{KO})_6(\text{HO})_6$
$6\text{WO}_3, \text{As}_2\text{O}_5, 4(\text{NH}_4)_2\text{O}, 2\text{H}_2\text{O} + 3\text{aq.}$	„ $\text{W}_6\text{As}_2\text{O}_{27}(\text{NH}_4\text{O})_6(\text{HO})_4 + 3\text{aq.}$
$16\text{WO}_3, \text{As}_2\text{O}_5, 6\text{Ag}_2\text{O} + 11\text{aq.}$	„ $\text{W}_{16}\text{As}_2\text{O}_{47}(\text{AgO})_{12} + 11\text{aq.}$

H. W.

**Yellow Incrustation from the Vesuvian Lava of 1631.** By A. SCACCHI (*Gazzetta*, **II**, 487).—The author in his more recent researches on this incrustation (comp. Abstr., 1880, 445) has found the resemblance between vesbium and vanadium to be so close as to make him believe that they are identical, or at least very closely allied. There are, however, differences in the properties of some of its compounds from those of vanadium, and the results of the analyses of the silver salt would seem to give a molecular weight for vesbium considerably greater than that of vanadium. The author intends to make more decisive experiments to ascertain the identity or non-identity of vesbium and vanadium, and remarks that even if the element should prove to be vanadium, it is an important fact that the presence of the latter in volcanic lavas has been established.

C. E. G.

## Mineralogical Chemistry.

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**Occurrence of Native Sulphur in the Soil of Paris.** By M. DAUBRÉE (*Compt. rend.*, **92**, 1440).—During the construction of a public sewer in the Rue Meslay, Paris, the workmen came across what appeared to be an ancient dustheap, extending for more than 50 meters in length and 4·5 meters in depth. It consisted of all sorts of vegetable and animal refuse, mixed with vast quantities of bones and plaster rubbish. The plaster, which was embedded in a black matrix, was uniformly impregnated with crystallised native sulphur, whilst the bones were filled in their interior with crystalline acicular gypsum. There can be no doubt but that this natural production of sulphur results from the action of the organic matter on the substance of the plaster, and that it therefore faintly resembles the contemporaneous formation of sulphur in many stratified rocks. That it was not due to the action of coal-gas was evident from its position, since it occurred at a much greater depth than the level of the gas-pipes, and

was not observable except in the neighbourhood of the organic rubbish before mentioned. J. W.

**Iron Ore, containing Manganese, from the Neighbourhood of St. Petersburg.** By N. LJUBAVIN (*Journ. Russ. Chem. Soc.*, 1882, 79—82).—The clay ironstone in question contains considerable quantities of manganese. Its analysis gave the following numbers:—Sand and residue insoluble in HCl and  $\text{Na}_2\text{CO}_3$  solution = 9·67;  $\text{SiO}_2$  soluble in  $\text{Na}_2\text{CO}_3$  = 4·27—

$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{MnO}_2$ .	$\text{MnO}$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{H}_2\text{O}$ and org. matter (by diff.).
5·52	48·54	15·86	5·90	0·67	0·11	9·16

The origin of the ore is due to the proximity of a mineral spring, rich in iron, which passes through a soil containing granite-sand. The orthoclase found in this granite contains manganese, as is seen from the following analysis made by Regel in the same laboratory:—

$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{MnO}$ .	$\text{CaO}$ .
64·21	17·37	0·91	0·48	0·66	1·20
$\text{MgO}$ .	$\text{K}_2\text{O}$ .	$\text{Na}_2\text{O}$ .	Loss on ignition.		
0·87	9·07	4·81	0·25		

Another sample gave 0·36 MnO. The red colour of such orthoclase is therefore not entirely due to  $\text{Fe}_2\text{O}_3$ . B. B.

**Minerals from Chili.** By J. DOMEYKO (*Jahrb. f. Min.*, 1882, 1, Ref., 165).—(1.) *Yellow Saltpetre containing Iodine and Chromium*.—Raymondi in Lima (1880) described a yellow saltpetre called by the miners “caliche azufrado” or sulphuretted saltpetre. He believed it to contain potassium monochromate, and called it “Tarapacaité.” According to Domeyko, this salt is found, not only at Tarapaca in Peru, but also in the salt-beds of the Atacama Desert, and in those of Carmen (Mejillones). It is fine-grained, light yellow, and occurs in the midst of very small-grained white saltpetre, usually passing gradually into the latter. At Cachinal in the Atacama Desert, it occurs in spherules 2—3 mm. in diameter in the midst of white saltpetre. In the salt-beds of Tarapaca the kidney-shaped lumps of tarapacaité are sometimes coated with a darker-coloured crust consisting, according to E. Williams, chemist to the mines, of potassium dichromate. Williams is also of opinion that the chromium is derived from beds of chrome-iron ore in the mountains by which the salt-beds are surrounded, inasmuch as the yellow and red salts are found only in the neighbourhood of these mountains. The salt is very deliquescent, and liable to change by exposure to the air, so that the analyses of different samples of it are by no means accordant. The freshest specimen analysed in Iquique by Williams contained 1·15 per cent.  $\text{Cr}_2\text{O}_3$ ; the analyses made by Domeyko on comparatively fresh material gave on the average only 1·18 to 0·52  $\text{Cr}_2\text{O}_3$  (mean 0·31);



together with 4.18 iodic acid, 10.03 chlorine, 2.10 sulphuric acid, 34.10 nitric acid, 8.45 potash, 27.60 soda, small quantities of lithia, lime, and magnesia, 7.05 hygroscopic, and 7.40 crystal-water, and 2.9 to 3.4 insoluble earthy residue. Altogether the "caliche azufrado" appears to be a variable mixture of several salts, resulting from the action of solutions containing chromium on crude Chili saltpetre.

*Huantajaité*.—Raymondi, in his "Minerales del Perú" (1878), describes this mineral as crystallising in small cakes, united in thin crystalline crusts, also fibrous and massive; brittle; having the appearance of rock-salt; colourless or white, not altered by exposure to light; less hygroscopic than common rock-salt; melting without decrepitation. Splinters moistened with water or with the tongue swell up slightly, and become white and opaque. It dissolves in water, with milky turbidity, due to the separation of silver chloride. The proportion of silver chloride in different specimens was found to vary from 3.1 to 5.6. The mineral is found on the Cerro de Huantajaya, three leagues from Iquique and about 1000 meters above the sea-level.

H. W.

**Vanadate of Lead and Copper from Laurium.** By F. PISANI (*Compt. rend.*, 92, 1292—1293).—Many simple and complex lead vanadates are known, such as *vanadinite*, *dechenite*, *eusynchite*, *aræoxene*, *motttramite*, and others. Of these, vanadinite and dechenite are simple vanadates, whilst the other contain a certain quantity of zinc or copper, sometimes both; aræoxine contains in addition arsenic acid.

The lead-copper vanadates are of a brown or olive-green colour, yielding a citron-yellow powder. A fine specimen of this latter mineral has been found by the author at Laurium. It occurs in a more or less crystalline condition as an incrustation on quartz, of a deep greenish-black colour when well crystallised, but paler coloured when the crystalline structure is less evident. The crystals under any circumstances are very small, though well defined, but their form could not be satisfactorily made out. Before the blowpipe it melts and gives off water; with the addition of sodium carbonate it is easily reduced. It is soluble both in hydrochloric and nitric acids. As it was impossible to separate the mineral wholly from the gangue, its density was not taken; its analysis gave the following results:—

V <sub>2</sub> O <sub>5</sub> .	PbO.	CuO.	CaO.	H <sub>2</sub> O.
25.53	50.75	18.40	1.53	4.25 = 100.46
11.1	3.64	3.72	0.59	3.70 = oxygen ratio.

These numbers lead to the ratio 5 : 3.3 between the oxygen of the vanadic anhydride and that of the bases. This is the same ratio as exists in *eusynchite* and *tritochlorite*, if the small proportion of lime and water be taken as derived from the gangue. It would be then a cupreous *eusynchite*, but containing equal equivalents of lead and copper, as in *psittacinite* and *motttramite*.

J. W.

**Mineralogical Notes.** By A. FRESNEL (*Jahrb. f. Min.*, 1882, 1, Ref., 193—196).—(1.) *Vanadinite* and *Tritochlorite*.—Brown spherules of vanadinite, from Wanlockhead, gave in two analyses the following results:—

	<i>a.</i>	<i>a</i> <sub>1</sub> .	<i>b.</i>	<i>b</i> <sub>1</sub> .	
Cl.....	2·28	2·54	2·42	2·48	
PbO.....	72·09	73·97	73·46	74·22	
CaO.....	2·94	3·02	3·17	3·25	
ZnO.....	0·08	—	0·59	—	
CuO.....	0·15	—	—	—	
Fe <sub>2</sub> O <sub>3</sub> .....	0·46	—	1·78	—	
Al <sub>2</sub> O <sub>3</sub> } .....	1·85	—			
SiO <sub>2</sub> } .....					
P <sub>2</sub> O <sub>5</sub> .....	2·68	2·75	2·86	2·93	
V <sub>2</sub> O <sub>5</sub> .....	(17·47)	17·92	(16·72)	17·12	
	100	100	100	100	

*a* and *b* are the direct results of analysis; *a*<sub>1</sub> and *b*<sub>1</sub> show the composition of the mineral after deduction of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZnO, CaO, and Fe<sub>2</sub>O<sub>3</sub>. The phosphoric acid is present, not as lead phosphate, but as calcium phosphate, isomorphously mixed.

*Tritochlorite*, a new mineral, is massive, of cauline structure, and somewhat distinctly cleavable in the longitudinal direction, parallel to a face corresponding with a pinacoid. The crystalline system is therefore probably rhombic, monoclinic, or triclinic. Colour, blackish-brown, with lighter yellowish-brown spots. Streak, pale lemon-yellow. H. = 3·5. G. = 6·25. Melts very easily, and with intumescence, before the blowpipe, giving off a faint arsenical odour; forms on charcoal in the oxidising flame a white and yellow incrustation of zinc oxide and lead oxide, and yields in the reducing flame globules of lead and a black porous mass. Dissolves in acids. Gives by analysis 53·90 PbO, 7·04 CuO, 11·06 ZnO, 24·41 V<sub>2</sub>O<sub>5</sub>, and 3·76 As<sub>2</sub>O<sub>5</sub> = 100·17, which is the composition of a tribasic vanadate. Tritochlorite differs from euxenite and aræoxene by its amount of copper and of arsenic. Locality, Mexico or South America.

(2.) *Minerals from Albergaria velha, in Portugal.*—The mines of Braçal, near Albergaria velha, are situated in a very large basin of clay-slate, and are worked for galena, with which are associated zinc-blende and wurtzite, pyrites and marcasite, dolomite and calcite.

(3.) *Picrosmine* occurs in the greenstone of the Plötlachthal, above Haslau, near Zwickau. It has a greenish-grey to mountain-green colour, and cauliform structure, and cleaves readily in a longitudinal direction. H. = 3. G. = 2·8. Lustre slightly fatty. Under the microscope it appears fine-fibred throughout. Dried at 100° it gave by analysis:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	H <sub>2</sub> O.
60·45	0·50	6·34	1·25	26·01	5·05 = 99·60
59·80	0·12	6·30	3·30	25·18	5·40 = 100·10

Before the blowpipe it burns white, and melts in thin splinters. When breathed upon it emits a bitter odour.

(4.) *Topaz, Gilbertite, Potassium-mica.*—The gilbertite of the Saxo-Bohemian tin-veins is not a distinct species, but merely a transition-product of the conversion of topaz (or of lithium-mica) into potassium-

mica. The topaz becomes white and greenish, and the product is called gilbertite. This latter then becomes laminar and light-coloured, and changes into potassium-mica. The pseudomorphosis of potassium-mica after topaz is not mentioned by Blum.

(5.) *Mealy Quartz*.—The cacochlor of the Saxon Obergelbige is accompanied by amethyst, which partly becomes soft and friable, and is sometimes even reduced to very fine powder having a sp. gr. of 2.645; it therefore consists not of tridymite but of quartz. Analysis gave 97.35 per cent. silica.

(6.) *Lautite*, a new mineral from the Rudolfschacht mine, at Laut, near Marienberg, has a metallic lustre, iron-black colour, and black streak;  $H. = 3-3.5$ ;  $G. = 4.96$ . It is mild to slightly brittle; has a cauliform to granular structure: is massive, and cleaves but indistinctly. Before the blowpipe it decrepitates strongly, and melts readily to a shining globule, giving off an arsenical fume. Dissolves in nitric acid, the solution giving silver chloride with hydrochloric acid, and after supersaturation with ammonia, the arsenic reaction with magnesium sulphate. Gives by analysis 27.60 per cent. Cu, 11.74 Ag, 42.06 As, and 18.00 S, leading to the formula  $Cu_4AgAs_3S_6$ . Tschermak found in one specimen of lautite 33.54 per cent. Cu, 3.03 Ag, 0.44 Fe, 42.60 As, 0.58 Sb, and 18.57 S = 98.76; and in another, 7.78 per cent. silver; whence it may be inferred that the silver merely replaces a portion of the copper, so that the composition of the mineral may be represented by the formula  $CuAsS$ . Very small crystals of lautite were apparently rhombic, exhibiting the combination  $\infty P. \infty P\infty. 0P$ .

Lautite is remarkable for its very small proportion of sulphur, whereby it approximates to the group of arsenical pyrites; nevertheless its formula cannot be made to accord with that of the latter, on account of the absence of univalent metal. H. W.

**Liquid Carbonic Anhydride in Smoky Quartz.** By G. W. HAWES (*Sill. Am. J.* [3], 21, 203—209).—On the Gaseous Substances contained in the Smoky Quartz of Branchville, Connecticut. By A. W. WRIGHT (*ibid.*, 209—216); *Jahrb. f. Min.*, 1882, 2, Ref., 191).—Hawes points out the frequent occurrence of enclosures of liquid carbon dioxide in the smoky quartzes of many localities, as Pike's Peak, Colorado; White Plains, N. Carolina; Monte Sella and Fibbia, on the St. Gothard; and refers to the presence of organic compounds in these minerals, as observed by Forster (*Pogg. Ann.*, 1871, 143, 173). Especially rich in such enclosures is the smoky quartz from the pegmatite vein of Branchville, Conn., in which carbon dioxide, both in the liquid and in the gaseous state, occurs in very variable quantities, and associated in the same cavities with water. Exact observations were made on the changes of relative volume of liquid and gaseous  $CO_2$ , according to change of temperature. Especially remarkable is the observation that when the  $CO_2$  is present in both states, the bubble disappears and reappears at the same temperature, whereas when a bubble of  $CO_2$  is present in water, the temperature (110—114°) at which the bubble disappears in consequence of expansion of the water and absorption of the carbon dioxide, differs widely from the temperature (25°) at which the bubble returns.—The

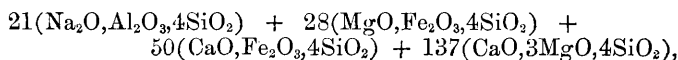
mobility of bubbles in liquid enclosures, whether they consist of carbon dioxide or of water, is attributed by Hawes to currents arising from changes of temperature, inasmuch as it was found possible, by keeping the temperature constant for a considerable time, to reduce even very lively bubbles to rest, or at least to diminish their mobility very considerably. On the other hand, bubbles at rest were thrown into motion on the approach of a source of heat.

Wright has made a chemical examination of the gases enclosed in the smoky quartz of Branchville, which has a sp. gr. of only 2·625—2·63. In one specimen he found the volume of these gases to increase to 1·65 times that of the enclosing quartz. The gases were collected by bursting small splinters of the quartz in an exhausted porcelain retort. The mean of two analyses, differing by only 0·01 from the values actually found, gave 98·33 CO<sub>2</sub> and 1·67 N, with traces of H<sub>2</sub>S, SO<sub>2</sub>, H<sub>3</sub>N, F, and Cl (?). The proportion of the enclosed gases to the water in the cavities is very nearly represented by the numbers 30·48 CO<sub>2</sub>, 0·50 N, and 69·02 H<sub>2</sub>O, in 100 volumes. H. W.

**Asbestos containing Sodium.** By MAX BAUER (*Jahrb. f. Min.*, 1882, 1, Mem., 158—161).—In a collection of Mexican minerals in the Mineral Cabinet of the Königsberg University, there is found, accompanying white massive quartz, a blue mineral forming tufts of long thin fibres, sprinkled with a white powder (calcium carbonate), which dissolves very easily in acids. The fibres are flexible, but not elastic, melt easily before the blowpipe; single fibres, even in a common candle flame, yielding a black magnetic glass. Sp. gr. 3·000 to 3·073. These characters are very much like those of crocidolite from South Africa. Analysis shows, however, that the two minerals are essentially distinct. The numbers found for the Mexican mineral were—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Na <sub>2</sub> O.	H <sub>2</sub> O.
55·48	2·01	12·32	10·35	17·23	1·54	1·47 = 100·40

which may be nearly represented by the formula



which is that of an amphibole. The Mexican mineral is therefore an asbestos especially characterised by containing soda, which has not hitherto been found in any true asbestos of the amphibole group. Crocidolite contains a much larger proportion of soda, less magnesia, no lime, and both oxides of iron, the total proportion of iron being large.

An asbestos containing soda in larger quantity than the preceding, has been found at Frankenstein in Silesia. This mineral forms a white mass, of sp. gr. 2·196, made up entirely of short bundles of separate fibres interwoven in various directions. The fibres hold together pretty strongly, and are elastically flexible, but break when too much bent. Before the blowpipe they melt easily to a white, not perceptibly magnetic glass. Imbedded in Canada balsam, they appear transparent

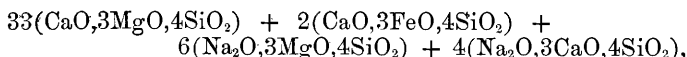
under the microscope, and in polarised light exhibit directions of extinction, varying between  $0^\circ$  and  $20^\circ$ . Analysis gave—

SiO <sub>2</sub> .	MnO.	FeO.	CaO.	MgO.	Na <sub>2</sub> O.	H <sub>2</sub> O <sup>(1)</sup> .	X <sup>(2)</sup> .
57.69	0.13	2.46	13.39	23.68	3.14	0.17	0.10 = 100.76

(<sup>1</sup>) Loss by ignition.

(<sup>2</sup>) Insoluble in HF.

The small amount of water is probably due to incipient weathering. Deducting this and the matter insoluble in hydrofluoric acid, the composition of the mineral may be approximately represented by the formula



which requires 56.35 SiO<sub>2</sub>, 2.24 (FeO, MnO), 13.73 CaO, 24.42 MgO, and 3.26 Na<sub>2</sub>O. H. W.

**Fayalite Slags from the Freiberg Furnaces, containing Zinc-spinell.** By A. STELZNER (*Jahrb. f. Min.*, 1882, I, Mem., 170—176).—The formation of zinc-spinell in the muffles of the Freiberg zinc-works has lately been described by Schulze (Abstr., 1881, 520), and the present paper gives an account of a similar formation, taking place with equal regularity in the slags produced in the smelting of lead ores at Freiberg. These slags consist mainly of a normal silicate, agreeing perfectly in its essential morphological and chemical constituents with that which is produced in numerous smelting processes in iron-works, and was shown by Mitscherlich, in 1882, to be of the nature of olivin or fayalite. In consequence, however, of the peculiar composition of the material smelted in the Freiberg furnaces, the fayalite of these lead-slags is not a pure ferrous silicate, but an isomorphous mixture of the latter with zinc silicate. Moreover, the slags vary in composition according to that of the mixture smelted and the mode of conducting the operation, but a general idea of their composition may be gained from Analysis I (p. 477).

The slags at the Freiberg works are left to cool in conical cast-iron crucibles, 58 cm. high and 50 cm. in their longer diameter, and solidifying to a compact mass of short prisms, having their axes perpendicular to the sides, and directed towards the centre of the crucible. This mass has ordinarily a dark greenish or brownish-grey colour and dull lustre; but the zinc fayalite which separates in it and constitutes the principal part of the slag, acquires, after a few days' exposure to the air, a dark steel-grey to iron-black colour, and semi-metallic lustre, and sometimes exhibits bright surface-colours. It is then easily seen to be developed in the form of thin crystalline plates, sometimes parallel to one another, sometimes without definite arrangement. During the solidification, eruption-cones, as much as 12 cm. high, sometimes form on the free surfaces of the slag-crucible; in other cases, namely, in the remelting of the lead-slags, these pseudo-volcanoes are not observed; but in the interior of the slag-crucibles—probably in consequence of a contraction going on simultaneously with the solidification—geodes are formed, sometimes

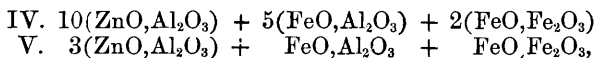
10 or 15 cm. in diameter, and filled with a cellulo-laminar aggregation of rectangular plates, having usually a maximum length of 10—15 mm. on the edge, and a fraction of a millimeter thick, a few, however, having a diameter of 40, and a thickness of 5—6 mm. Analysis II gives the composition of such a lamino-cellular filling material of the central geode of a slag-crucible from the Muldner works. III shows the composition of native fayalite from Fayal.

	I.	II.	III.
SiO <sub>2</sub> .....	20·7	28·45	29·15
SnO <sub>2</sub> .....	—	0·75	—
PbO.....	3·9	2·50	1·55
CuO .....	1·2	0·60	0·31
FeO.....	48·8	41·98	60·95
MnO .....	1·4	—	0·69
ZnO.....	14·4	18·55	—
Al <sub>2</sub> O <sub>3</sub> .....	2·5	1·31	4·06
CaO.....	3·9	3·00	0·72
MgO .....	1·2	0·84	2·38
BaO.....	0·3	1·80	—
S.....	4·1	1·70	—
Deduct for S.....	2·0	0·85	—
	100·4	100·63	99·81

The fayalite crystals are accompanied by more or less opaque grains and lamellæ, apparently consisting of metallic sulphides.

The lead-slugs also contain a yellowish-red isotropic substance, the chemical nature of which has not yet been determined, together with thread-like groups of small crystals, having very much the appearance of certain Bryozoa (cellepores, &c.); and the author especially recommends the study of these lead-slugs to those who hastily infer the existence of remains of organisms, from similar appearances in crystalline rocks which have been solidified from fused magmas.

Another constant constituent of the Freiberg lead-slugs is a zinc-spinell, which occurs imbedded in the large fayalite crystals, in the form of small, perfectly developed octohedrons, mostly isolated, sometimes in small groups. Their chemical composition is somewhat variable, different specimens giving by analysis the numbers IV and V in the following table, leading to the formulæ IV and V:—



which give the percentages IV\* and V\* :—

	IV.	IV.*	V.	V.*
ZnO.....	27·21	27·21	25·24	25·24
FeO.....	—	12·77	—	15·27
Fe <sub>2</sub> O <sub>3</sub> .....	24·49	10·30	33·00	16·12
Al <sub>2</sub> O <sub>3</sub> .....	50·55	50·55	43·36	43·36
	102·25	100·83	101·60	99·99

The composition and structure of these lead-slugs exhibit but little variation, having been found to be nearly the same in the years 1874, 1879, and 1881.

Spinell appears to be formed also in other metallurgical processes. According to W. Muirhead (*Iron*, 15 Oct., 1880) aluminates of magnesia, or of lime and magnesia, are formed in the slags of Scotch blast-furnaces, whenever iron-ores rich in magnesia are smelted with fluxes rich in alumina, especially when the temperature of the furnace is high, the quantity of these aluminates varying from  $\frac{1}{2}$  to 18 per cent. accordingly as the smelting process goes on regularly or irregularly, and a very viscid slag being sometimes produced, to the great detriment of the yield of iron. These iron slags also vary considerably in composition, one specimen yielding, according to Muirhead's analysis, 23.41 MgO, 8.48 CuO, 68.11  $\text{Al}_2\text{O}_3$ ; and another, 31.08 MgO, and 68.92  $\text{Al}_2\text{O}_3$ , the latter agreeing pretty nearly with the composition of typical spinell (28.05 MgO and 71.95  $\text{Al}_2\text{O}_3$ ).

Finally the author suggests that these various modes of spinell-formation in metallurgic operations may throw considerable light on the formation of eruptive rocks, and especially on the occurrence of spinell in peridotites.

H. W.

**Artificial Orthoclase produced in the Wet Way.** By C. FRIEDEL and E. SARASIN (*Compt. rend.*, 92, 1374—1376).—The apparatus which was devised for the purpose of raising the reacting substances to the required temperature, consisted of a steel tube of 10 mm. thickness, and 15 mm. internal diameter, lined inside with copper or platinum. A copper or platinum stopper was made to close the interior tube, and a steel cap capable of being fastened down with screws fitted over the whole. The tube was placed in a block of cast iron, and heated with gas; in this way it was found possible to maintain easily a temperature approaching to dull redness.

The experiments of Daubrée on the decomposition of felspar by water, having shown that this mineral loses potassium silicate by contact with water, even at the ordinary temperature, it was obvious that if felspar was to be successfully produced in the wet way, it could only be in presence of excess of alkaline silicate. The mixture therefore which was used consisted of gelatinous silica, alumina, and solution of potash, but better results were obtained by precipitating potassium silicate with aluminium chloride, washing and pressing the precipitate, and then diffusing it in a strongly alkaline solution of potassium silicate. The heating under pressure was continued from 16 to 30 hours. With the first mixture at a moderate temperature, quartz was obtained in crystals sufficiently large to be measured with the goniometer. At a higher temperature, it was mixed with hexagonal plates of tridymite, which were easily recognisable by their grouping and want of action on polarised light; it is the first time that this mineral has been artificially produced in the wet way, although Rose succeeded in making it by fusing silica with microcosmic salt.

By using a mixture of aluminium silicate and potassium silicate, and diminishing gradually the proportion of silica, the quantity of quartz produced was much diminished, and a fine crystalline powder

obtained instead. This powder, separated from the finer portions by levigation, presented the following properties: it melted with difficulty before the blowpipe to a white glass; it was unattacked by acids; it had sensibly the density of orthoclase, as was ascertained by pouring a certain quantity into a solution of potassium iodomercurate, made of such a density that while orthoclase floated, quartz sank to the bottom. The powder of the artificial mineral floated in this liquid, and by the addition of a few drops of water at the top, so as to form layers of different densities, the powder remained at exactly the same level as did a natural specimen of orthoclase. On analysis, the silica was found to be rather too high, 70 to 72 per cent. instead of 64·6, but the ratio of the oxygen of the alumina to that of the potash was as 3 : 1. A microscopic examination showed that a portion of the silica existed as quartz, so that there was little doubt but that the mineral operated on consisted of orthoclase mixed with a little quartz, nevertheless it is still possible that the artificial felspar may be of a composition analogous to petalite rather than to orthoclase; unfortunately the microscopic examination does not permit the proportion of quartz to be determined with sufficient exactness to enable the question to be decided.

The remainder of the communication is taken up with the crystallographic measurements of the mineral in question. J. W.

**Artificial Production of Analcime.** By A. DE SCHULTEN (*Compt. rend.*, 94, 96—97).—When sodium silicate and aluminate are mixed in such proportions that the ratio of silica to alumina is the same as in analcime, and the mixture heated with lime-water at 180° for 18 hours in a closed copper tube, crystals of analcime are obtained. These are sometimes cubes, sometimes trapezohedrons of the cubic system, but more frequently combinations of the two forms. Trapezohedrons are apparently formed when the solution is highly concentrated and strongly alkaline, cubes being formed under the opposite conditions. The lime-water simply facilitates the formation of distinct crystals. The crystals obtained in this manner have no action on polarised light; the natural crystals have optical properties similar to those of the quadratic system; the optical properties of the crystals obtained by the author by heating a solution of sodium hydroxide in sealed glass tubes, would place them in the rhombic system. Hence it would appear that the elementary crystals of analcime are subject to slight changes in their axes of elasticity, sufficient to affect their optical symmetry, but not sufficient to prevent the large crystals having forms belonging to the cubic system. C. H. B.

**Notes on Italian Minerals.** By A. CORSI (*Jahrb. f. Min.*, 1882, 1, Ref., 187—189).—Tuscan Zircon.—A. From Figline (Prato). Occurs, imbedded together with apatite, sphene, actinolite, prehnite, epidote, magnetite, and pyrites, in a coarsely-grained euphotide (gabbro), in separate crystals having adamantine lustre, and reddish-yellow to greenish colour or nearly colourless. Forms: P, 3P3, ∞P, ∞P∞, occurring either altogether or only the first three. Axial ratio  $a : c = 1 : 0·6395$ . The crystals are 5—10 mm. long, and 2 mm. thick, seldom larger. Many exhibit a scaly structure, so that their cleavage



parallel to the faces P and  $\infty P \infty$  is imperfect. Sp. gr. = 4.593 for impure and turbid, 4.655 for transparent crystals; H. = 7.5. Strong positive double refraction. Before the blowpipe, and with reagents, they exhibit the usual characters of zircon. Analysis gave 33.11 per cent.  $\text{SiO}_2$ , 66.82  $\text{ZrO}_2$ , 0.35  $\text{Fe}_2\text{O}_3$ , traces of CaO and  $\text{MgO}$ , and 0.43 loss by ignition; the formula  $\text{ZrO}_2.\text{SiO}_2$  requiring 32.97 per cent.  $\text{SiO}_2$  and 6.7  $\text{ZrO}_2$ . Under the microscope the transparent zircon appears relatively pure; it sometimes exhibits fluid cavities and a number of irregular, sometimes rectilinear cracks; only very thin sections exhibit bright polarisation-colours. The green zircon contains a greenish substance enclosed.

*B. Zircon from the Granite-veins of Elba.*—A thoroughly decomposed granite-vein containing tourmalins, at La Fate near San Piero, yielded a few highly lustrous, very small, dark yellow-red or greenish octohedral crystals, which proved to be zircon. Small crystals of zircon have also been obtained from the vein of Grotta d'Oggi and of Facciatoja near San Piero.

The green crystals from La Fate, of somewhat more frequent occurrence than the reddish-yellow, exhibit the forms P and  $\infty P \infty$ , sometimes quite in the form of the garnet-octohedron; they are very small, and often have re-entering angles at their edges, like crystals of harmotome. They are sometimes implanted on albite and orthoclase. Lustre fatty to adamantine. Translucent to transparent. Infusible. H. = 7.

The green crystals from Grotta d'Oggi are small, and occur very rarely on lepidolite. They are slightly transparent and have a fatty lustre. Their form, like that of the crystals from La Fate, resembles a garnet octohedron, so that they might be mistaken for green garnet, as was perhaps the case with the so-called green garnet from the same locality mentioned by G. vom Rath and others. But their infusibility and many other properties which were examined, preclude the idea of their being garnet; moreover, some of their angles which have been measured agree with those of zircon. Nevertheless, it is quite possible that true garnets may occur in the same locality.

The green crystals from Facciatoja, implanted on albite, agree perfectly with those just described.

The zircon of Elba is distinguished from that of all other localities by the fact that the crystals are implanted on the sides of geode-cavities, not imbedded in the rock.

The Italian localities of zircon now known are the following: (1.) The auriferous sand of Ticino, near Bernato, Buffalora, &c., where it is associated with hyacinth. (2.) In the Venetian territory, near Brendola, in a conglomerate, together with grains of sapphire; at Leonedo in volcanic sand, together with corundum; and in the pitchstone of the Euganean Hills. (3.) In the bombs of Somma. (4.) In the sands on the shores of the Tyrrhenian Sea, particularly numerous and well-formed crystals being found at the mouth of the Volturno. (5.) In the gabbro of Figline near Prato. (6.) In the geodes of the granites of Elba.

Black Spinell (Ceylanite or Pleonast) in the Greenstones of Elba.—Occurs in geodes in the greenstones of Monte Capanne, and in

black octohedrons destitute of metallic lustre in a diorite near S. Ilario. Some of the crystals consist of O alone; others have their edges truncated by  $\infty$ O. In size they vary from very small dimensions to 2 cm. Sp. gr. = 3.582 to 3.812 at 27°; mean 3.697. H. = 7 to 8. In all their other properties they agree with ceylanite; also in their formula  $(\text{Mg}, \text{Fe})\text{O} + (\text{Al}_2, \text{Fe}_2)\text{O}_3$ . H. W.

### Chemical Composition of Metaxite from Reichenstein.

By MAX BAUER (*Jahrb. f. Min.*, 1882, 1, Mem., 161—163).—Metaxite from Schwarzenberg in Saxony and Reichenstein in Silesia has hitherto been regarded, according to closely agreeing analyses by Delesse and by Kuhn, as a non-aluminiferous silicate having the composition of serpentine, and therefore as a variety of the latter. The analysis of a greenish-white mineral, called metaxite, from Pregratten in Tyrol, cited by G. Bischoff (*Chem. u. physikal. Geologie*, 2, 305), also gave the composition of a serpentine, viz., 42.19  $\text{SiO}_2$ , 38.71  $\text{MgO}$ , 5.98  $\text{FeO}$ , 0.6  $\text{Al}_2\text{O}_3$ , and 12.54  $\text{H}_2\text{O}$ . Different results have, however, lately been obtained by R. B. Hare (*Zeitschr. f. Kryst.*, 3, 294), according to whose analysis, metaxite from Reichenstein contains a large quantity of alumina, and has a composition altogether different from that of serpentine, viz., 43.87  $\text{SiO}_2$ , 23.44  $\text{Al}_2\text{O}_3$ , 5.37  $\text{Fe}_2\text{O}_3$ , 1.24  $\text{CaO}$ , 15.18  $\text{MgO}$ , 10.86  $\text{H}_2\text{O}$  = 99.96. From this analysis (and from other considerations) Hare regards this serpentine as originating from felspar. To account for the difference between his own results and those of Delesse and Kuhn, he supposes that the latter relate, not to metaxite, but to chrysotil, which he also finds to be free from alumina, and to have the composition of serpentine. To decide between these conflicting views, the author selected from the mineral collection of the Königsberg University some very pure specimens of metaxite from Reichenstein, having in the air-dried state a density of 2.549, and agreeing in external characters with those described by Hare. An analysis by Friederici of this mineral, dried at 100°, gave the following results:—

$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{H}_2\text{O}$ .	$\text{Na}_2\text{O}, \text{Li}_2\text{O}$ .
42.73	trace	2.79	0.40	40.37	12.17	1.52 = 99.98,

agreeing nearly with the formula of serpentine,  $3\text{MgO}, 2\text{SiO}_2, 2\text{H}_2\text{O}$ , which requires 43.48 per cent.  $\text{SiO}_2$ , 43.48  $\text{MgO}$ , and 13.04  $\text{H}_2\text{O}$ . Part of the water is expelled at a much higher temperature than the rest. The analysis shows that pure metaxite from Reichenstein is not a transition-form between serpentine and felspar. H. W.

**Volcanic Rocks of Easter Island (Rapa-Nui).** By C. VELAIN (*Jahrb. f. Min.*, 1882, 1, Ref., 241).—This island, the most easterly of the Australian group, contains numerous colossal busts, the works of an extinct race, which have been chiselled with tools of obsidian out of a trachytic rock, or a volcanic breccia, occurring on the island. One of the latter kind was conveyed to Paris in 1872, and set up in the court of the Musée d'Histoire Naturelle, where it is undergoing complete disintegration by the action of wind and rain. A fragment of it which had fallen was examined microscopically by the author, and found to be made up of lumps of the size of a walnut, consisting of

basalts and augite-andesites, containing large quantities of glassy substance. All these fragments in the volcanic breccia of Easter Island are cemented together by a vitreous substance allied to sideromelane and palagonite. The palagonite and sideromelane of this locality contain, as original constituents, magnetite and opal-sphærolites, whereas in all other respects, they agree with the types previously examined. Analysis I shows the composition of the dark brown sideromelane glass; II, that of the yellow palagonite, which, however, could not be completely freed from sideromelane:—

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	
I.	49·67	14·46	18·52	7·23	3·74	2·92	1·64	1·17	= 99·35
II.	40·12	13·27	10·65	9·47	3·32	2·06	0·97	20·43	= 100·29
									H. W.

**Studies on Monte Somma.** By J. ROTH (*Jahrb. f. Min.*, 1882, 1, Ref., 229).—The lavas of Somma are, in all essential particulars, identical with those of Vesuvius, and the veinstones of Somma, like those of Vesuvius, consist of leucite-basanites. The following table exhibits the total constituents (soluble and insoluble in hydrochloric acid) of:—I. The lava of Cisterna. II. Pumice from the tufa-covering of the Cisterna lava. III. A dense stream-rock, above the Casa dell' Acqua in the Capo dell' Olivello valley. IV. Lava-stream in the Vallore di Castello. V. Rock of the vein Primo Monte at the upper end of the Fossa Vetrana. VI. Rock of a vein, 1 meter broad, in the Canale di Forciella. VII. Light-grey finely porous veinstone of the Canale dell Arena:—

	I.	II.	III.	IV.	V.	VI.	VII.
SiO <sub>2</sub> .....	49·44	52·22	51·42	47·54	50·39	53·98	52·74
Al <sub>2</sub> O <sub>3</sub> .....	14·96	19·85	21·34	18·38	19·43	17·44	19·96
Fe <sub>2</sub> O <sub>3</sub> .....	3·52	3·32	5·38	5·16	3·83	4·11	1·75
FeO.....	9·07	2·55	4·29	11·35	7·10	2·47	8·57
MgO.....	4·74	2·31	0·26	0·84	2·33	0·46	1·06
CaO.....	10·88	6·24	9·34	8·38	9·13	15·67	8·92
Na <sub>2</sub> O.....	1·99	5·52	2·55	2·35	2·45	2·48	2·67
K <sub>2</sub> O.....	5·41	6·37	3·77	5·15	4·91	2·02	4·47
Loss by ignition.	—	1·96	0·28	0·43	0·80	—	0·66
	100·01	100·34	98·63	99·58	100·37	98·63	100·80

Especially remarkable in these analyses is the frequently small amount of magnesia, in spite of the amounts of olivin and augite contained in the rocks.

Another point of interest is the occurrence—rare indeed—of old massive rocks enclosed in the tufa of Somma; thus Roth found in the surface-layers of the tufa in the Vallone Piscinale near Ottagana, a lump of syenite of the size of the fist. Lastly, it may be noticed that the rock of a lava-stream on the lower declivity of Monte Croce, Rocca Monfina, which was regarded by Abich as related to dolerite (sp. gr. = 2·7952: SiO<sub>2</sub> = 54·62), is really a felspathic basalt-lava,

so that in this remarkable crater, with its circumvallation of leucite and its central hills of trachytic rocks, the presence of basalt is now positively established. H. W.

**Examination of Chinese and Japanese Rocks used for the Manufacture of Porcelain.** By W. PABST (*Jahrb. f. Min.*, 1882, 1, Ref., 231).—The material used in China for the manufacture of porcelain is obtained from layers of phyllite, and is derived from helleflinta-like deposits therein, the felspathic constituent of which has been converted wholly or partially into a micaceous mineral (potash-mica) frequently occurring in splendid microscopic pseudomorphs after orthoclase and plagioclase. The “small clayslate needles” of the phyllites, in which are imbedded the helleflinta-like rocks used for the porcelain manufacture, are regarded by Kalkowsky as staurolite.

The raw material used for the porcelain manufacture in Japan is obtained from the neighbourhood of Arita, Province of Hezen, in Japan, and appears to consist of elastic acid eruptive masses of tertiary age, containing a large proportion of potash-mica, probably due to the action of later eruptions. In addition to the potash-mica, these tufas and breccias contain quartz, amorphous substances, and fragments of liparites, perlites, obsidian, andesites, trachytes, and sandstones. H. W.

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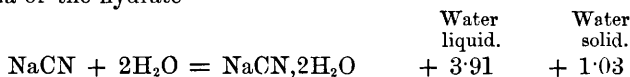
## Organic Chemistry.

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**Sodium and Barium Cyanides.** By M. JOANNIS (*Compt. rend.*, 92, 1338—1341).—The sodium cyanide was made by adding hydrocyanic acid to soda dissolved in absolute alcohol: the sodium cyanide is precipitated. Washed with alcohol and dried in a vacuum, it forms a white crystalline powder. The heat of solution of the anhydrous cyanide in 100 parts of water at 9° was found to be  $-0.5$  unit, which gives for the heat of formation of the cyanide—

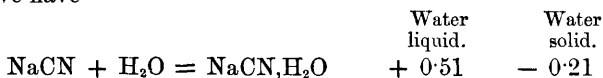


*Hydrates.*—This cyanide forms with water two hydrates, viz.,  $\text{NaCN}, 2\text{H}_2\text{O}$  and  $\text{NaCN}, \text{H}_2\text{O}$ . The former is made by dissolving the anhydrous cyanide in alcohol, boiling at 75°; on cooling, the hydrate crystallises out in thin layers: in a vacuum over sulphuric acid, it loses all its water. The heat of solution under the same circumstances as before was  $-4.41$  units, whence it is possible to conclude for the formula of the hydrate—



The second hydrate is obtained by evaporating an alcoholic solution of the first-mentioned hydrate in presence of lime to absorb only the vapour of water. It gradually deposits in crystals, which are per-

factly free from alcohol. The heat of solution was  $-1.01$  units, from which we have—

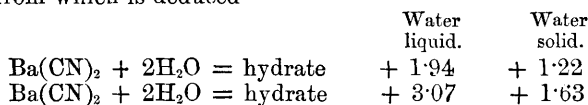


It is singular that the heat of formation of this hydrate should be less than that of the hydrate containing  $2\text{H}_2\text{O}$ ; the contrary being generally the case.

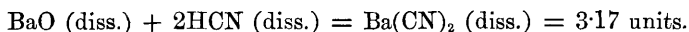
*Barium Cyanide.*—The precipitate obtained by the action of hydrocyanic acid on alcoholic solution of baryta is of variable composition, generally containing considerable quantities of barium alcoholate.

*Hydrates.*—Hydrocyanic acid mixed with crystallised baryta in aqueous solution, forms a solution which, by evaporation in a vacuum, yields white crystals, very deliquescent, and rapidly absorbing carbonic anhydride from the air. This composition was found to be  $\text{Ba}(\text{CN})_2, 2\text{H}_2\text{O}$ .

This hydrate loses a molecule of water in a vacuum over sulphuric acid, leaving the hydrate  $\text{Ba}(\text{CN})_2, \text{H}_2\text{O}$ . The method of preparing the anhydrous salt is not given in this memoir. The heat of dissolution of these three salts in 100 parts of water at  $6^\circ$  was as follows:— $\text{Ba}(\text{CN})_2 = +0.89$ ;  $\text{Ba}(\text{CN})_2, \text{H}_2\text{O} = +1.05$ ;  $\text{Ba}(\text{CN})_2, 2\text{H}_2\text{O} = -2.88$  units; from which is deduced—

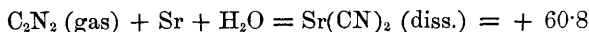


A further determination gave—



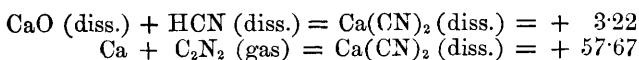
These numbers are very similar to those obtained by Berthelot for the hydrates of barium chloride and bromide. J. W.

**Strontium, Calcium, and Zinc Cyanides.** By M. JOANNIS (*Compt. rend.*, 92, 1417—1419).—*Strontium cyanide* was prepared by the action of strontium hydrate and hydrocyanic acid. It is not very stable, and could not be obtained in the anhydrous form. Its hydrate has the composition  $\text{Sr}(\text{CN})_2, 2\text{H}_2\text{O}$ . Heat of dissolution of this hydrate in 100 parts of water at  $8^\circ = -2.07$  units, and heat of formation of strontium cyanide  $+3.135$  units; consequently—



*Calcium cyanide* could not be isolated either in the anhydrous or hydrated form, but it was easily prepared in concentrated solution by the action of lime on hydrocyanic acid.

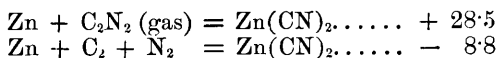
At  $7^\circ$  the following numbers were obtained:—



*Zinc cyanide* is prepared by precipitating a solution of zinc acetate by hydrocyanic acid, and the precipitate, dried at  $100^\circ$ , is pure

and anhydrous. It may, however, be obtained in a crystalline form by arranging solutions of zinc acetate, water, and hydrocyanic acid in order of their respective densities in a tall jar; the zinc cyanide crystallises after some time in orthorhombic prisms.

The solution of 1 mol. of zinc cyanide in dilute hydrochloric acid disengages at  $12^{\circ} + 1.7$  units, from which may be deduced—



The heat of formation could not be determined by precipitating a salt of zinc by potassium cyanide, because the precipitation is never complete. J. W.

**Potassium Chromocyanide.** By H. MOISSAN (*Compt. rend.*, **93**, 1079—1081).—When chromous acetate is mixed with a small quantity of an aqueous solution of potassium cyanide in a closed vessel at ordinary temperatures, much heat is developed and a deep red precipitate is formed, which floats on the surface of a yellowish liquid. If the potassium cyanide is in excess, the precipitate is green and the liquid deep yellow. On allowing it to stand for a week, long yellow needles separate out, and these are purified by crystallisation. The same compound is obtained by the action of potassium cyanide on chromous chloride; by heating pulverulent chromium with a concentrated solution of potassium cyanide in sealed tubes at  $100^{\circ}$ ; by the action of potassium cyanide on chromous carbonate. Potassium chromocyanide forms yellow macled crystals, often of considerable size, unchanged on exposure to air at ordinary temperatures: sp. gr. = 1.71. They are anhydrous, and have the composition  $\text{K}_4\text{CrC}_6\text{N}_6$ . At  $20^{\circ}$ , 1 c.c. of water dissolves 0.3233 gram of salt: the saturated solution gives total absorption of the violet, more feeble absorption of the blue, and three distinct bands in the green. When the aqueous solution is boiled for some time, a small quantity of hydrocyanic acid is given off, and chromium sesquioxide deposited. The salt has no action on polarised light. It has a taste similar to that of potassium ferrocyanide, and resembles the latter in its physiological action. When electrolysed, it gives chromicyanide at the positive pole, and hydrogen and potassium hydroxide at the negative. Heated to dull redness out of contact with air, it fuses, then gives off nitrogen, leaving a residue of chromium carbide and potassium cyanide. With dilute sulphuric acid, it gives hydrocyanic acid; with the strong acid, carbonic oxide. Oxidising agents convert the yellow potassium chromocyanide into red chromicyanide,  $\text{K}_3\text{CrC}_6\text{N}_6$ . The chromocyanide gives no precipitate with alkalis or alkaline sulphides, and usually no precipitates with salts of metallic acids. With salts of manganese, zinc, and cadmium, it forms white precipitates: with silver and lead salts, yellow precipitates; with chromous salts, a blackish precipitate. With ferrous salts it gives an orange-red precipitate which becomes ochreous. This reaction is characteristic.

C. H. B.

**Etherification of Alcohols and Acids of Double Function.** By N. MENSCHUTKIN (*Journ. Russ. Chem. Soc.*, 1882, 62—79).—

(a.) *Formation of ethereal salts of "alcohol-acids"* (hydroxy-acids of the fatty series). Although the acid-function of such compounds has been thoroughly investigated by Würtz and Friedel, this is not the case with regard to their alcoholic character. The action of free acid on alcohol-acids seems to have first been investigated by the author. With isobutyl alcohol and lactic acid, three reactions take place, the two first being reversible, viz. (1) formation of isobutyl lactate and water; (2) of lactide and water; and (3) probably partial conversion of the lactide into the ethereal salt. The action of acetic acid is similar. Probably even more complicated reactions take place. The author investigated three typical cases: *glycollic acid*, as a primary alcohol and primary acid; *lactic acid*, as a secondary alcohol and "secondary" acid; and *dimethyl-oxalic acid* as a tertiary alcohol and tertiary acid.

*Glycollic Acid*.—Instead of acting on isobutyl alcohol with glycollic acid, the author started from glycollide. Equivalent quantities of glycollide, isobutyl alcohol, and water gave, on heating at  $155^{\circ}$  in a sealed tube, the limit 67·67 (percentage of neutralised acid). On replacing the alcohol with acetic acid, the limit 49·22 was obtained. A mixture of glycollide and water gave the limit 32·40 as expression of the "inner" etherification of glycollic acid. If more water is present, the limit is lower.

*Lactic Acid*.—Under similar circumstances, lactide water, and isobutyl alcohol gave the limit 68·01; lactide, acetic acid, and water, 56·48. The limit of "inner" etherification of lactic acid (1 mol. to  $\text{H}_2\text{O}$ ) is 32·16, and it diminishes with increasing quantity of water.

*Dimethyl-oxalic Acid*.—Isobutylic system: rate of etherification (during the first hour) = 40·56; limit = 64·61. Acetic acid system: limit very low, about 12·06 (in 312 hours). Inner etherification, limit = 10·83.

The limits of etherification of alcohol-acids (isobutylic systems) are nearly the same as in the corresponding system of saturated monobasic acids:—

	Limits.
Isobutyl-acetic system .....	67·38
Isobutyl-glycollic system .....	67·67
Isobutyl-propionic system .....	68·70
Isobutyl-lactic system .....	68·01

The function of an acid is therefore the same, if one hydrogen-atom is replaced by the hydroxyl-group. The limits of "inner" etherification are only about half as great as those of isobutylic systems, as if the molecules of the alcohol acids were composed of half a molecule of an alcohol and half a molecule of an acid. The limits of etherification in acid systems become lower if one hydrogen-atom of an alcohol is replaced by the carboxyl-group. The acid and "inner" etherification of dimethyl-oxalic acid as a tertiary-tertiary alcohol acid is very small, and this is analogous to the incapability of tertiary alcohols for forming ethereal salts (as Menschutkin found before). In all the above cases the author assumes that no secondary reactions take place.



Experiments of a similar kind with other alcohol-acids, as glyceric, tartaric, citric acids, did not succeed because these acids decompose when heated for some time.

*Quinic acid* shows in the isobutylic (alcohol) system a high value for the rate of etherification in the first hour, viz., 72·23, with 75·74 as a limit. The limit of the acetic acid system is = 61·14; that of inner etherification = 55·19. From these high values (as compared with dimethyloxalic acid), the author concludes that quinic acid is neither a tertiary acid nor a phenol acid, as in the last-named kind of acids no inner etherification takes place.

(b.) *Phenol Acids*.—Salicylic acid is decomposed on heating, and therefore only the rates of etherification (after one hour) could be determined. The values for both the isobutylic and the acetic systems (the last for methylsalicylic acid) are very small, salicylic acid being a tertiary acid.

Instead of parahydroxybenzoic acid anisic acid was used. The rate of etherification is 5·31, the limit 71·44 in the isobutylic system. *Meta-hydroxybenzoic acid*.—No inner etherification takes place. The rate of etherification in the isobutylic system is = 4·54, the limit 70·86. The low limit for the acetic system = 7·04, characterises this acid as a phenol acid. (N.B.—In the above paper the author describes lactic acid as a type of secondary alcohol and secondary acid. Seeing that in lactic acid the carbon of the carboxyl-group is united with a *primary* carbon-atom, it would seem that lactic acid does not fulfil the conditions required in secondary acids.)

B. B.

**Rectification of Alcohols.** By E. MAUMENÉ (*Bull. Soc. Chim.* [2], 36, 653).—A reply to some observations of Naudin (*Bull. Soc. Chim.* [2], 36, 273).

**Normal Ethyl Sulphate.** By N. STEMPNEVSKY (*Jour. Russ. Chem. Soc.*, 1882, 95—99).—Two bodies corresponding with the empirical formula  $C_4H_{10}SO_4$  can exist, one being the normal ethyl sulphate and the other the ethyl salt of isethionic acid. Neither has hitherto been obtained synthetically by the action of ethyl iodide on the silver salts of the corresponding acids. The first compound was obtained by Wetherill in 1848, by the action of sulphuric anhydride on ethylic ether. In 1876, Mazurowska, by the action of sulphuryl chloride on absolute alcohol, obtained a compound, which she thinks is normal ethyl sulphate, and which is different from the ethyl salt of Wetherill, of which only small quantities are formed at the same time.

By the action of ethyl iodide in ethereal solution on isethionate of silver, the author obtained a compound which, on decomposition with water, gave isethionic acid, and was therefore ethyl isethionate. Silver sulphate and ethyl iodide under similar circumstances gave a liquid of sp. gr. 1·167, with an odour of peppermint, and leaving a greasy spot on paper; it could be only partly distilled without decomposition. On heating it with water, ethyl alcohol, and sulphuric and ethyl-sulphuric acids are formed. This compound is identical with that obtained by Wetherill, and described as normal ethyl sulphate, but

different from the "neutral ethyl sulphate" of Mazurowska, the nature of the last-named compound remaining unexplained.

B. B.

**Diallyl-ethyl-carbinol.** By A. SMIRENSKY (*J. pr. Chem.* [2], **25**, 59—60).—This tertiary alcohol,  $C(C_2H_5)_2Et.OH$ , is prepared from ethyl propionate by the method used for the preparation of diallyl-methyl-carbinol and diallyl-propyl-carbinol. It is a colourless liquid, similar in odour to its homologues; b. p.  $175-176^\circ$  at  $743.5$  mm. pressure; sp. gr.  $0.8776$  at  $0^\circ$ ,  $0.8637$  at  $17^\circ$ , the coefficient of expansion between these temperatures being  $0.00095$ . On oxidation with alkaline permanganate, it yields oxalic acid and another acid not yet identified.

A. J. G.

**Preparation of Aldol.** By A. WURTZ (*Compt. rend.*, **92**, 1438—1439).—Although the preparation of aldol is a comparatively easy operation, there are several precautions which it is important to notice, as the yield and quality of the product depend upon a variety of circumstances, which can otherwise be ascertained only by experience.

The following are the details of an operation. 2 kilos. of aldehyde and 2 kilos. of water having been introduced into 2 kilos. of hydrochloric acid, the mixture was left alone for three days at a temperature of  $15^\circ$ . At the expiration of this time, the liquid, which was of a brownish-yellow colour, was neutralised with sodium carbonate and exhausted several times with ether, whereby 100 grams of a product boiling below  $85^\circ$  in a vacuum were obtained, 495 grams of aldol boiling between  $85^\circ$  and  $105^\circ$ , and 100 grams of a residue boiling between  $105^\circ$  and  $180^\circ$  at 10 mm. pressure. The aldol thus obtained was very fluid at first, but it soon became hot spontaneously and changed to a very thick colourless syrup, wholly soluble in water. During the neutralisation, a small quantity of resinous matter separated.

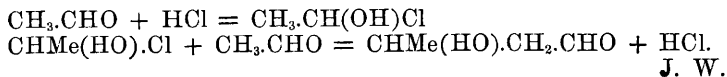
Two kilos. of the same aldehyde, treated as before with dilute hydrochloric acid, but allowed to stand for eight days, became darker coloured, and when neutralised deposited a large quantity of black resin, together with a slightly coloured crystalline substance. By exhaustion with ether, the liquor yielded 320 grams of aldol boiling from  $85^\circ$  to  $105^\circ$ , and 70 grams of a product boiling between  $105^\circ$  and  $190^\circ$  at 10 mm. pressure.

The resin methodically exhausted with boiling water, furnished 117 grams of dialdane.

In a third operation with 2 kilos. of aldehyde, when the mixture stood for 12 days, only 75 grams of aldol were obtained, and this was apparently mixed with a good deal of crotonic aldehyde, as manifested by its odour and imperfect solubility in water. Such an aldol breaks up easily into crotonic aldehyde and water, for on heating it on a water-bath it gradually disappears, evolving a strong odour of the aldehyde during evaporation.

The theory of the formation of aldol is as follows: The hydrochloric acid attaches itself first to the aldehyde, and the chlorhydrin thus

obtained reacting on a second molecule of aldehyde forms aldol, and regenerates the hydrochloric acid, thus :—



**New Alcohol from Daldane.** By A. WURTZ (*Compt. rend.*, **92**, 1371—1374).—Daldane is a condensation product of aldol, containing the elements of 2 mols. of aldol, minus 1 mol. of water,  $2(\text{C}_4\text{H}_8\text{O}_2) = \text{C}_8\text{H}_{14}\text{O}_3 + \text{H}_2\text{O}$ . It is a body with mixed functions, being at once aldehyde, secondary alcohol, and ether. By oxidation, it yields a well crystallised monobasic acid,  $\text{C}_8\text{H}_{14}\text{O}_4$ , and by hydrogenation the alcohol which is the subject of the present memoir.

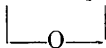
A dilute aqueous solution of daldane is treated with a large excess of a 1 per cent. sodium-amalgam, the solution being kept slightly acid; at the expiration of some time, the liquid is carefully neutralised and evaporated to a syrupy consistence. The sodium chloride is got rid of by the addition of absolute alcohol, the latter evaporated, and the syrup distilled in a vacuum: a large portion of the product passes over between  $160^\circ$  and  $175^\circ$  at 10 mm. pressure. It is a thick colourless liquid, very thick, solidifying to a mass of crystals after standing some days. 50 grams of daldane yielded 25 grams of liquid boiling at the above temperature, and a semi-solid residue which could not be distilled.

The purified crystals are colourless, deliquescent, soluble in all proportions in water and alcohol, and very soluble in ether. They soften at  $49^\circ$ , and are completely melted at  $53^\circ$  to a colourless liquid, boiling at  $162\text{--}165^\circ$  under 10 mm. pressure. Analysis showed it to have the formula  $\text{C}_8\text{H}_{14}\text{O}_3$ , that is, 1 mol. of daldane has fixed 2 atoms of hydrogen. Its alcoholic character was established by preparing its aceto-compound by the action of acetic anhydride; this, when purified and analysed, had the composition  $\text{C}_8\text{H}_{14}\text{Ac}_2\text{O}_3$ ; the determination of the acetic acid by saponification with baryta also led to the same formula.

Both nitric acid and phosphorus perchloride attack the new alcohol with great violence; but by the moderated action of the latter, a chloride has been obtained which remains to be examined.

The aqueous solution of the alcohol does not reduce silver nitrate, neither does the body assimilate water when heated to  $150^\circ$  with dilute sulphuric acid.

If dialdol be represented by the normal constitutional formula  $\text{CH}_3.[\text{CH}(\text{OH}).\text{CH}_2]_3.\text{CHO}$ , we may reasonably assume that daldane will have the formula  $\text{CH}_3.\text{CH}.\text{CH}_2.\text{CH}.\text{CH}_2.\text{CH}(\text{OH}).\text{CH}_2.\text{CHO}$ , the



alcohol will then differ from the latter only in having the  $\text{CH}_2.\text{OH}$  group in place of the aldehydic grouping  $\text{CHO}$ . As the new alcohol fixes neither bromine nor hydrogen, the above hypothesis, which shows it to be at the same time a primary, a secondary alcohol, and an ether, is also in accordance with facts.

J. W.

**The Reducing Substance formed by the Action of Potassium Hydroxide on Grape-sugar.** By A. EMMERLING and G. LOGES (*Pflüger's Archiv.*, **24**, 184—188).—In a paper in the *Ber.*, **6**, 22, one of the authors described his investigations on the reducing power of acetol. The present investigation was intended to determine whether the smell produced in the application of Trommer's test was due to this body, as it has a close resemblance to it. A body was obtained from the mixture which, however, proved not to be acetol, though probably a ketone-alcohol; as yet the authors have not succeeded in preparing it pure. W. N.

**Inversion of Sugar by Carbonic Anhydride.** By E. MAUMENÉ (*Bull. Soc. Chim.* [2], **32**, 652).—The author again calls attention to the fact that the maximum inversion of sugar is much greater than the number given by Biot,  $38^\circ$ , and is at least  $42^\circ$ . With carbonic anhydride under pressure, Lippmann has obtained the number  $44^\circ$ , and the same result may probably be obtained with very dilute sulphuric and other acids. The author considers that the levulose studied by Jungfleisch and Lefranc is probably very different from that of inverted cane-sugar. *Inactose* may be easily obtained by the action of equal weights of normal sugar and silver nitrate in concentrated solution. It is a distinct species, and must not be confounded with inverted sugar, which is inactive in consequence of the relative proportions of dextrose and levulose which it contains. C. H. B.

**Compounds of Carbohydrates with Alkalis.** By T. PFEIFFER and B. TOLLENS (*Annalen*, 285—309).—These compounds are very unstable, and the composition varies with the mode of preparation; by repeated washings, they continue to lose small amounts of alkali, but by adopting an identical method of preparation and treatment, the authors have obtained results from which fairly accurate conclusions as to the molecular weights of the carbohydrates may be drawn. The sodium compounds are obtained by adding an alcoholic solution of sodium ethylate to the carbohydrate triturated with water; the sodium compound is precipitated by means of alcohol, and after dissolving in water precipitated by alcohol again. The product obtained was dried at  $96$ — $98^\circ$ , and the sodium determined in it by decomposing it with excess of titrated sulphuric acid, and estimating the free acid by titration with baryta-water in presence of rosolic acid. The potassium compounds were prepared by using an alcoholic solution of potash; in these cases also the product obtained by two precipitations with alcohol was regarded as the purer compound. These compounds are decomposed by carbonic anhydride, and hence they always contain small amounts of potassium or sodium carbonate.

The sodium compound with starch contains 3.44 per cent. of sodium, corresponding to either  $C_{24}H_{39}O_{20}Na$  (3.43 per cent. Na) or  $C_{24}H_{41}O_{22}Na$  (3.34 per cent. Na). The potassium compound contains 5.25 per cent. of potassium, which is the mean of the percentages of potassium calculated for the formulæ  $C_{24}H_{33}O_{20}K$ ,  $C_{24}H_{41}O_{22}K$ ,  $C_{30}H_{49}O_{25}K$ . From the analyses of these compounds the authors conclude that the molecular formula for starch is either  $C_{24}H_{40}O_{20}$ , or  $C_{24}H_{42}O_{21}(C_{24}H_{40}O_{20} + H_2O)$ .

According to this formula, the amount of dextrose obtained from starch must be 108.11 per cent., and its conversion is expressed as follows:  $C_{24}H_{42}O_{21} + 3H_2O = 4C_6H_{12}O_6$ . This is more in accordance with the results of Sachsse than if the old formula  $C_6H_{10}O_5$  be taken.

*Cane-sugar*.—The sodium-compound of cane-sugar is more stable than the corresponding starch-compound; the amount of sodium varies from 6—8 per cent., showing its molecular formula to be smaller than that of starch; the formula  $C_{12}H_{21}O_{11}Na$  corresponds to 6.32 per cent. Na, and the sodium, after seven precipitations of the compound, sank to 6.25 per cent.

*Inulin*.—The analyses of the sodium and potassium compounds of this substance show that its formula must be either  $C_{12}H_{20}O_{10}$  or  $C_{12}H_{22}O_{11}$ .

*Dextrin*.—The results obtained with this substance, although not very satisfactory, serve to indicate the fallacy of the formula  $C_6H_{10}O_5$ , and that its molecular weight more nearly approximates to that of the saccharoses than that of amyloses.

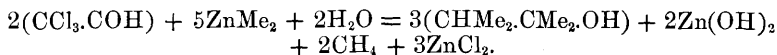
*Amylodextrin*.—The sodium compound prepared from the crude amylodextrin has a composition similar to the starch-compound, whereas the compounds obtained from amylodextrin prepared from the crude product, indicate that by the means adopted it is resolved into more simple substances, corresponding more or less with dextrin, inulin, and cane-sugar.

P. P. B.

**Elementary Composition of Glycogen.** By M. ABELES (*Pflüger's Archiv.*, **24**, 485—488).—Külz and Borntraeger having objected to the author's formula for the compound of glycogen with barium,  $C_{18}H_{30}O_{16}Ba$ , explains that in burning the compound in a stream of oxygen, some of the  $CO_2$  remains behind as barium carbonate. The author finds glycogen prepared by his zinc chloride method as pure as that obtained by Brücke's process.

W. N.

**Action of Zinc Methide on Chloral.** By B. RIZZA (*Journ. Russ. Chem. Soc.*, 1882, 99—103).—By acting with zinc methide on chloral, the formation of butyl- (tertiary) methyl-carbinol was expected, but since, instead of this, dimethyl-isopropyl-carbinol was obtained, an intramolecular change must have taken place. The first and last phases of the reaction are represented by the equation:—



The properties of the alcohol obtained agree with those found by Pawloff (*Ann.*, **196**, 221) for dimethyl-isopropyl-carbinol. The boiling point was found by the author to be 117—120°. With phosphorus pentachloride it gave the chloride  $C_6H_{13}Cl$ , and yielded acetone and acetic acid on oxidation. With hydriodic acid and potash, hexylene (b. p. 73°) was obtained, the dibromide of which melts at 168—169°, so that the hexylene is tetramethyl-ethylene.

B. B.

**Action of Caustic Alkalis on Acetone Solutions of Halogenated Compounds.** By C. WILLGERODT (*Ber.*, **14**, 2451—2460).

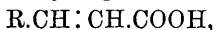
—When finely powdered potassium hydroxide is added to a mixture of equal parts of acetone and chloroform, a violent action sets in; when the action ceases after sufficient potassium hydroxide has been added (about 20 per cent. of the acetone), the clear supernatant liquid is poured off from the solid potassium chloride, which is exhausted with ether, and the two liquids are mixed. On distilling with steam, the unattacked substances pass over first, and are again treated with potassium hydroxide; the ether exerts no injurious effect. On fractionally distilling the residue in the retort, a white crystalline solid is obtained (b. p.  $167^{\circ}$ , uncorr., m. p.  $96-97^{\circ}$ ), smelling like camphor. This *acetonechloroform*,  $\text{COMe}_2\text{CHCl}_3$ , as the author calls it, distils readily with steam, and sublimes even at the temperature of the human body. If a small piece is thrown on water, in which it is insoluble, it will rotate for a long time; it is easily soluble in ether, alcohol, glacial acetic acid, acetone, and chloroform, and crystallises very well from these solutions. Concentrated nitric and sulphuric acids dissolve and decompose it when warm, the latter even in the cold, with evolution of hydrochloric acid. It burns with a green flame. It reduces ammoniacal silver solution after some time.

The corresponding reaction with bromoform and acetone is more violent; the product *acetonebromoform* is similar to *acetonechloroform*, it melts at  $167^{\circ}$ , and has a sharp peppery odour. Carbon tetrachloride, acetone, and potassium hydroxide, yield a body crystallising in long colourless needles, which have a pleasant odour and are extremely soluble in alcohol and ether. By similar treatment, benzoic chloride, methyl iodide, and ethyl iodide, yield pleasant-smelling liquids which have not yet been thoroughly examined.  $\alpha$ -Dinitrochlorobenzene gives a solid crystallising from alcohols in long needles (m. p.  $48^{\circ}$ ). With aniline, it forms red needles of  $\alpha$ -dinitrophenylaniline.

D. A. L.

**Halogenised and Hydroxylised Organic Acids.** By E. ERLMEYER (*Ber.*, 14, 1318—1321).—In this paper, the author gives some general conclusions respecting the orientation of the halogen- and hydroxyl-radicles in organic acids, deduced partly from his own observations on the substitution-products of the acids  $\text{R}'\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ , and the addition-products of the unsaturated acids  $\text{R}'\cdot\text{CH}:\text{CH}\cdot\text{COOH}$ , partly from those of Michael and Norton (*Abstr.*, 1881, 798) on the monobromocrotonic acids, and those of Mauthner and Suida (*ibid.*, 889), on the brominated propionic and acrylic acids.

(1.) When in an acid  $\text{R}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ , 1 atom of hydrogen is replaced by bromine, the bromine generally goes into the  $\alpha$ - or the  $\beta$ -position, accordingly as the reaction takes place at a temperature not exceeding  $100^{\circ}$ , or above it.—(2.) When a mono-halogenised acid is formed by the addition of a hydrogen-haloid,  $\text{HR}$ , to an acid



the greater part of the halogen goes into the  $\beta$ -position, the smaller part frequently into the  $\alpha$ -position. (3.) When an  $\alpha$ -halogenised acid is heated with water and a base, the product consists wholly of the  $\alpha$ -hydroxy-acid; with alcoholic solutions, however, the  $\alpha$ -ethoxy-acid

thus formed is accompanied by a small quantity of an unsaturated acid. When, on the other hand,  $\beta$ -halogen-acids are heated with water or aqueous bases, there are formed—together with carbonic acid and so-called unsaturated hydrocarbons—chiefly unsaturated acids, with smaller quantities of  $\beta$ -hydroxy-acids. With alcoholic solutions, the product consists almost wholly of unsaturated acids. (4.)  $\alpha$ -Hydroxy-acids, heated with saturated solutions of haloid acids, are resolved for the most part into aldehyde and formic acid, with only a small quantity of  $\alpha$ -hydroxy-acid. (6.)  $\beta$ -Hydroxy-acids similarly treated are first resolved into water and unsaturated acids, which then take up a hydrogen-haloid in the manner above mentioned. (7.) When dehalogenised acids are formed by substitution of 2 at. Br for 2 at. H, both the bromine-atoms, at least in the case of propionic and butyric acids, go into the  $\alpha$ -position. (8.) On the addition of bromine to  $R.CH:CH.COOH$ , at a comparatively low temperature, and with exclusion of water, one bromine-atom goes into the  $\alpha$ -, the other into the  $\beta$ -position. (9.) The  $\alpha$ -dibrominated acids are but slowly attacked by boiling water, and, according to observations hitherto made only on  $\alpha$ -dibromopropionic and -butyric acids, a slight action seems to take place, resulting in the replacement of the two Br-atoms by two hydroxyl-groups, or 1 atom of oxygen. (10.) The  $\alpha\beta$ -dibrom-acids are decomposed by boiling water in the way known to take place with phenyldibromopropionic acid, a halogen-hydroxy-acid being formed, together with carbonic anhydride and a brominated hydrocarbon. Such halo-hydroxy-acids are also formed—generally in two isomeric modifications—by addition of  $HOBr$  or  $HOCl$  to unsaturated acids. Both these isomerides are converted by alkalis into glycidic acids, which then again take up a hydrogen-haloid in such a manner that the halogen goes into the  $\beta$ -position. (11.) The  $\alpha$ -dibrom-acids are less easily attacked by alcoholic potash than the  $\alpha\beta$ -acids, yielding  $\alpha$ -brominated unsaturated acids, and with excess of potash also non-brominated acids (propionic acid). (12.) The  $\alpha\beta$ -dibrom-acids treated with alcoholic potash give up  $HBr$  in two directions, chiefly  $\beta$ -bromine and  $\alpha$ -hydrogen, the product therefore consisting in this case also mainly of  $\alpha$ -brominated unsaturated acid.

The remainder of the paper is taken up with a discussion of Mauthner and Suida's views on the constitution of the bromacrylic acids.

H. W.

**Action of Haloid Acids on Ethereal Salts.** By E. SAPPER (*Annalen*, 211, 178—213).—It has long been known that the presence of halogen acids materially assists the formation of ethereal salts, and conversely, that the same acids decompose the salts, with formation of halogen derivatives of the hydrocarbon. The author has carried on a series of experiments, in order to investigate the condition of either reaction.

**I. Decomposition of Ethereal Salts.**—Lautemann, Crafts, and Gal have shown that various ethereal salts are completely decomposed when heated with hydrobromic or hydriodic acids. In the present communication the author arrives at the following results:—(1.) Ethereal salts containing paraffinoid radicles are decomposed by haloid

acids (whether in the gaseous state or in solution) into the free acid and a halogen-compound of the radicle; but salts containing a phenylic group undergo a further decomposition. (2.) The action of the acid is at first most energetic, but soon decreases, so that a long time is required for the completion of the decomposition. (3.) As a final result, the action of the same haloïd acid on different ethereal salts is the same, but salts containing acid or alcoholic radicles of low molecular weight are decomposed rather more quickly than salts containing radicles of high molecular weight. (4.) The velocity of the action is greater the higher the molecular weight of the haloïd acid. Thus it follows from the experiments that if the difference of affinities between iodine and hydrogen, and iodine and the alcoholic radicles at  $100^{\circ}$ ,  $I,R-I,H$ , be taken as unity, then  $Br,R-BrH = \frac{1}{2.06}$ , and  $Cl,R-Cl,H = \frac{1}{985}$ .

II. *Etherification by Haloïd Acids*.—By the action of a haloïd acid on a mixture of an organic acid and an alcohol for a short time, the ethereal salt is formed, but this is again decomposed on heating. The author, by the light of these results, proceeds to examine the various theories which have been propounded to explain the action of the haloïd acid in the process of etherification. It is generally supposed that the acid acts simply as a dehydrating agent; but it is improbable that hydrochloric acid could remove 75 per cent. of the water required by theory from a mixture of alcohol and acetic acid, and on further heating, again give it up and reproduce 35 per cent. of the acetic acid originally used. The second theory, which supposes the formation of a halogen derivative of a hydrocarbon which reacts with the organic acid to form the ethereal salt and the haloïd acid has been refuted by Friedel, who showed that ethyl chloride and acetic acid do not form ethyl acetate; and the author has obtained the same result with ethyl bromide and iodide. The third theory proposed by Friedel supposes the formation of a haloïd anhydride of the acid, which reacts with the alcohol to form the ethereal salt. But although hydrochloric acid when passed into acetic acid forms no acetic chloride, yet this reaction can be effected in presence of some dehydrating agent, as phosphoric anhydride. To confirm Friedel's view, it is shown that by the action of acetyl bromide on alcohol in presence of water, over 54 per cent. of the alcohol is converted into the ethereal salt. Further, the fact that only a small quantity of haloïd acid is required to convert relatively large quantities of alcohol and acid into the ethereal salt also supports this view, the final change being the result of the following reactions (in which X represents the halogen):  $XH + Me.COOH + EtOH = Me.COX + EtOH + H_2O = Me.COOEt + XH + H_2O$ ; but on heating, the further change  $Me.COOEt + XH + H_2O = Me.COOH + EtX + H_2O$  predominates. V. H. V.

**Decomposition of Metallic Formates in Presence of Water.** By J. RIBAN (*Compt. rend.*, 93, 1023—1026, and 1082—1085).—A 2 per cent. solution of formic acid in water, when heated in sealed tubes at  $175^{\circ}$  for 24 hours, is partly decomposed, with production of



carbonic oxide, carbonic anhydride, and hydrogen, the last two being liberated in equal volumes.

5 per cent. aqueous solutions of metallic formates, when heated at  $175^{\circ}$  for 41 hours and upwards in sealed tubes from which all air has been removed, undergo more or less complete decomposition. Potassium, sodium, and barium formates are not decomposed, but those of ammonium, calcium, magnesium, manganese, iron, cobalt, nickel, zinc, tin (stannous), lead, copper, mercury (mercuric), and silver are partially split up into hydrogen, carbonic anhydride, carbonic oxide, and a metallic oxide or carbonate. The decomposition takes place most readily with the salts of zinc, lead, tin, copper, nickel, and cobalt. The oxides of nickel and cobalt are mixed with a large proportion of metallic nickel or cobalt, magnetic, and with a metallic lustre. In all probability the formates are first saponified by the water, with formation of a metallic oxide, and liberation of formic acid. The latter is then decomposed into hydrogen and carbonic anhydride, with small quantities of carbonic oxide. In certain cases the carbonic anhydride acts upon the metallic oxide, producing a carbonate: this secondary reaction diminishes the proportion of carbonic anhydride in the liberated gases. In the case of lead formate, lead carbonate is formed in crystals identical with those of cerusite.

When an aqueous solution of cupric formate is boiled with free exposure to air, formic acid is liberated, and a green crystalline powder, insoluble in water, is thrown down. This when dried at  $100^{\circ}$ , has the composition  $\text{Cu}(\text{CHO}_2)_2 \cdot 2\text{CuH}_2\text{O}_2$ . By prolonged boiling with water it is decomposed, with evolution of carbonic anhydride, and formation of cuprous oxide. Heated with water at  $100^{\circ}$  in a closed tube free from air, cupric formate is decomposed, thus:  $2\text{Cu}(\text{CHO}_2)_2 + \text{H}_2\text{O} = \text{CO}_2 + \text{Cu}_2\text{O} + 3\text{H}_2\text{CO}_2$ . The cuprous oxide is deposited in a crystalline form, a small quantity is reduced to metallic copper, and a small quantity of hydrogen gas is liberated, but no carbonic oxide. When the liquid is heated at  $175^{\circ}$ , carbonic anhydride is at first liberated, in accordance with the preceding equation, but after a time the products formed react on one another. In contact with the cuprous oxide, the formic acid is decomposed, thus:  $\text{CO}_2 + \text{Cu}_2\text{O} + 3\text{H}_2\text{CO}_2 = \text{H}_2 + 2\text{CO}_2 + \text{Cu}_2\text{O} + 2\text{H}_2\text{CO}_2$ , and on further heating this decomposition tends to a maximum, in accordance with the equation  $\text{H}_2 + 2\text{CO}_2 + \text{Cu}_2\text{O} + 2\text{H}_2\text{CO}_2 = 3\text{H}_2 + 4\text{CO}_2 + \text{Cu}_2\text{O}$ . At this point the decomposition of the formic acid is complete, and almost the whole of the copper is in the form of cuprous oxide, only traces having been reduced to the metallic state. On further heating, however, hydrogen gas disappears, and the cuprous oxide is completely reduced.

The cuprous oxide produced by this decomposition forms brilliant violet cubes and octohedrons; the metallic copper is sometimes crystallised in square prisms terminated by square pyramids, belonging apparently to the quadratic, but in reality to the regular system.

The author finds that in presence of cuprous oxide, dilute formic acid is completely decomposed when heated in sealed tubes for 24 hours, at  $175^{\circ}$ , and that cuprous oxide is completely reduced by hydrogen when heated with this gas and water in sealed tubes at the same temperature.

Mercuric formate in aqueous solution is decomposed at  $175^{\circ}$ , in accordance with the equation  $\text{Hg}(\text{CHO}_2)_2 = \text{CO}_2 + \text{H}_2\text{CO}_2 + \text{Hg}$ . This is the only case in which no hydrogen is liberated, a result probably due to the fact that the metallic mercury is liquid.

Silver formate is decomposed at  $100^{\circ}$ , with liberation of formic acid and deposition of metallic silver; at the same time a small quantity of hydrogen is given off, owing to the action of the acid on the metal. At  $175^{\circ}$ , the formic acid is completely split up into carbonic anhydride and hydrogen. The greater part of the silver deposited is in a crystalline form. The author finds that dilute formic acid is completely split up by heating with finely divided silver under similar conditions.

C. H. B.

### Decomposition of Metallic Formates in Presence of Water.

By BERTHELOT (*Compt. rend.*, **93**, 1051—1054).—The author shows that all the decompositions studied by Riban are exothermic reactions, and that the phenomena observed are in perfect accord with the laws of thermo-chemistry. Metallic silver probably facilitates the decomposition in the same manner as platinum, by lowering the temperature required. In the decomposition of formic acid in presence of cuprous oxide, a trace of cuprous formate is possibly formed as an intermediate product, just as silver oxide is formed in the decomposition of hydrogen peroxide by metallic silver.

C. H. B.

**Theory of Formates.** By MAUMENÉ (*Compt. rend.*, **94**, 79—82).—The author endeavours to show that the results obtained by Riban are in perfect agreement with his *general theory*.

C. H. B.

**Methylethylacetic and Hydroxymyristic Acids in the Essential Oil of the Fruit of the Angelica Archangelica.** By R. MÜLLER (*Ber.*, **14**, 2476—2484).—Two varieties of oil were used, one old, brown, and viscid (sp. gr. 0.9086), the other freshly distilled, amber-coloured, and mobile (sp. gr. 0.8549; refrac. index, 1.4855). The former contained 5, the latter 10 per cent. oxygen; both had a feeble acid reaction; there was no further noteworthy difference between them. They distilled between  $174$ — $300^{\circ}$ , leaving about 11 per cent. residue, the greater part passing over between  $176$ — $280^{\circ}$ . As fractional distillation did not answer as a means of separation, the entire distillate was treated with alcoholic potash; and, as soon as the reaction was complete, a stream of carbonic anhydride was passed through it, the greater part of the alcohol distilled off, the residue shaken with water, and the *oily layer* separated from the solution of the potassium salt. The acid obtained by decomposing this potassium salt has the odour of valeric acid, and a strongly acid reaction; it is a colourless oil, which does not solidify even in a freezing mixture, and boils somewhere about  $170$ — $176^{\circ}$ ; numbers from analysis point to the formula  $\text{C}_5\text{H}_{10}\text{O}_2$ , or rather to a mixture of 3 mols. of this body with 1 mol.  $\text{C}_5\text{H}_{10}\text{O}_2 + \text{H}_2\text{O}$ ; and as the barium salt does not crystallise, this, the author thinks, must be *methylethylacetic acid*, for all the other acids isomeric with this form crystalline barium salts. The acid reaction of the oil is probably due to this acid being present in the free state. It is

rather peculiar that angelic acid is found in the roots of this plant, whilst methylethylacetic acid is found in the fruit.

The residue from the distillation is treated with alcoholic potash, then with carbonic anhydride, the alcohol distilled off, the residue extracted with warm water, and the solution acidified with dilute sulphuric acid; the acid separated in this way is then purified by repeated solution in sodium carbonate and reprecipitation with sulphuric acid, and recrystallisation from alcohol. It forms white leaflets, with mother-of-pearl like lustre (m. p.  $51^{\circ}$  C.), insoluble in water, but easily soluble in alcohol; the solution has an acid reaction. Analysis suggests that this is *hydroxymyristic acid*,  $C_{14}H_{28}O_3$ , and the subsequent experiments support this view. The *potassium salt*,  $C_{14}H_{27}KO_3 + H_2O$ , crystallises from alcohol in warty aggregations, soluble to a small extent in cold, but very easily in hot water. The solution has a neutral reaction, froths when shaken, makes the skin feel slippery, and when concentrated to a certain degree sets to a jelly. The salt is precipitated from its solution by sodium chloride and potassium carbonate. The solution gives precipitates with barium, calcium, zinc, lead, silver, copper, mercury, and iron salts. The *silver salt*,  $C_{14}H_{27}AgO_3$ , is a white, bulky precipitate, which soon blackens when exposed to light. The *calcium salt*,  $(C_{14}H_{27}O_3)_2Ca$ , is also a white bulky precipitate, slightly soluble in cold, completely in hot water, from which solution it crystallises in tufts of microscopic needles. The *barium salt*,  $(C_{14}H_{27}O_3)_2Ba$ , is a white flocculent precipitate, sparingly soluble both in hot and cold water. The *lead salt*,  $(C_{14}H_{27}O_3)_2Pb$ , is a white flocculent precipitate, only slightly soluble in hot, and insoluble in cold water. The *copper salt*,  $(C_{14}H_{27}O_3)_2Cu$ , is a green bulky precipitate, insoluble in water. These salts show that the acid is monobasic. When this acid is heated with benzoic chloride in a sealed tube, hydrochloric acid is evolved, and *benzoylhydroxymyristic acid*,  $C_{14}H_{27}BzO_3$  is formed; it crystallises in small white leaflets (m. p.  $68^{\circ}$ ), soluble in alcohol; the solution has a strongly acid reaction. The *sodium salt* forms white flocks, soluble in hot water. The *silver salt*,  $C_{14}H_{26}BzAgO_3$ , is a white precipitate, which blackens on exposure to light. The formation of this last acid is a proof that this fixed acid of the essential oil of angelica contains a hydroxyl group.

The colourless neutral oil above referred to is a terpene,  $C_{10}H_{16}$  (b. p.  $172.5^{\circ}$ ; sp. gr. 0.8487; refrac. index, 1.481; vap. dens. found, 63.9), which on slow oxidation in the air and light, gave the ozone or peroxide reaction and formic acid. A terpene hydrate and hydrochloride of constant composition could not be obtained.

D. A. L.

**Reduction of Succinic Chloride, and on Normal  $\gamma$ -Hydroxybutyric Acid.** By A. SATZFEFF (*J. pr. Chem.* [2], 25, 61–72).—By reducing succinic chloride with sodium, the author obtained a substance which he described as succinic aldehyde (this Journal, 1874, 570). He now admits the correctness of the statement of Hennert

and Bredt, that it is in reality *butyrolactone*,  $\begin{array}{c} CH_2-CO \\ | \\ CH_2-CH_2 \end{array} > O$ . It boils at  $206^{\circ}$  (corr.), has sp. gr. 1.1441 at  $0^{\circ}$ , and 1.1286 at  $16^{\circ}$ , the expan-

sion coefficient between these temperatures being 0.00086. On heating it with baryta-water, it yields normal  $\gamma$ -hydroxybutyric acid, this acid again yielding the lactone when distilled.

Normal  $\gamma$ -hydroxybutyric acid is a non-crystallisable liquid; it volatilises with water-vapour, has a feebly acid reaction, readily unites with metallic oxides, but cannot be completely saturated by carbonates, with the exception of those of the alkalis. The *potassium* salt can be obtained as a fibro-crystalline mass; the *sodium* salt forms indistinct groups of needles; the *ammonium* salt crystallises from alcohol in globular aggregates; all three salts are deliquescent. The *zinc* salt forms an indistinctly crystalline mass.

By heating butyrolactone with phosphorous iodide, iodobutyric acid is formed, which, by treatment with sodium amalgam in acid solution, may be converted into normal butyric acid. A. J. G.

**Abnormal Crystals of Citric Acid.** By C. CLOEZ (*Bull. Soc. Chim.* [2], 36, 648—650).—When chlorine gas is passed into a solution of citric acid in  $1\frac{1}{2}$  parts of water at  $100^\circ$ , chloracetone and hydrochloric acid are formed. After passing the gas for 8 or 10 days, the solution on standing deposits crystals of considerable size. These are long, flat quadrilateral prisms, of the composition,  $\text{H}_5\text{C}_6\text{O}_7\text{H}_3 + 2\text{H}_2\text{O}$ , but very different in appearance from the short regular crystals of commercial citric acid. This difference is due to the abnormal development of the faces on the obtuse angles of the fundamental prism. Measurements of the angles are given in the original paper. The crystals differ from those obtained by Marchand, by containing 2 mols.  $\text{H}_2\text{O}$ , instead of only 1 mol. The abnormal crystallisation is not due to the presence of hydrochloric acid; for the author finds that citric acid crystallises in its usual form from both dilute and concentrated hydrochloric acid. C. H. B.

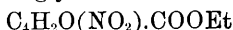
**Mucic Acid and Dehydromucic Acid.** By A. KLINKHARDT (*J. pr. Chem.* [2], 25, 41—59).—On carefully heating mucic acid at about  $280^\circ$ , a small quantity of yellow crystals of dehydromucic acid condenses on the neck of the retort, whilst pyromucic acid distils into the receiver. The best yield of dehydromucic acid was obtained by heating equal parts of mucic acid, concentrated hydrochloric acid, and hydrobromic acid in sealed tubes for eight hours at  $150^\circ$ . On boiling the product with a large quantity of water, diphenylene oxide passes over with the aqueous vapour. An aqueous solution of dehydromucic acid, when treated with ferric chloride, yields a transparent jelly.

*Dehydromucic chloride*,  $\text{C}_4\text{H}_2\text{O}(\text{COCl})_2$ , is prepared by slowly heating 1 mol. of dehydromucic acid with 2 mols. of phosphoric chloride. It has an odour like that of phosphoric oxychloride, is readily soluble in alcohol, ether, and chloroform, melts at  $80^\circ$ , and sublimes at about  $100^\circ$  in broad colourless needles. It would appear from this reaction that the oxygen in the radical is not present as hydroxyl. Dehydromucic acid is regenerated on treating the chloride with water.

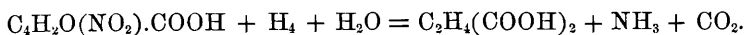
*Dehydromucamide*,  $\text{C}_4\text{H}_2\text{O}(\text{CONH}_2)_2$ , is obtained by acting with dry ammonia on an ethereal solution of dehydromucic chloride. It crystallises in fine white needles, does not melt at  $240^\circ$ , is readily soluble in hot water, nearly insoluble in ether and alcohol. The author was

not able to prepare dehydromucic anhydride, nor could he obtain either chlorinated or brominated derivatives of dehydromucic acid; bromine-water oxidises dehydromucic acid to fumaric acid.

*Nitropyromucic Acid*,  $C_4H_2O(NO_2).COOH$ .—On treating 1 part of dehydromucic acid with 1 part of sulphuric acid and 10 parts of hydrated nitric acid, nitropyromucic acid is obtained; it crystallises in fine clear yellow rectangular tables, melts at  $183^\circ$ , is readily soluble in alcohol and ether, sparingly in water. The *ethyl* salt,



(m. p.  $107^\circ$ ), crystallises in silky rhombic plates, and is decomposed by hot water. On reducing an aqueous solution of the acid with tin and hydrochloric acid, succinic acid, carbonic anhydride, and ammoniac chloride are obtained.



The statement that pyromucic acid gives a green coloration with ferric chloride is incorrect, this reaction being due to the isopyromucic acid which accompanies it. Pyromucic acid gives a reddish-brown precipitate with ferric chloride. In conclusion, the author calls attention to the similarity of relation between mucic, dehydromucic, and pyromucic acids on the one hand, and of citric, aconitic, and itaconic acids on the other.

A. J. G.

**Furfural.** By E. FISCHER (*Annalen*, **211**, 214—232).—The reaction whereby benzaldehyde is converted into benzoin, would seem to offer a ready method of synthesis of a hitherto almost uninvestigated class of bodies, the ketonic alcohols. But no such action takes place with the aldehydes of the acetic acid series, or with acetaldehyde, when they are heated with potassium cyanide, and of the aromatic series only anisic and cumic aldehydes yield homologues of benzoin. As furfural resembles benzaldehyde in its reaction with ammonia, and its conversion into an isomeride, furfuraline, so it yields compounds similar in constitution to benzoin.

*Furoin*,  $C_{10}H_8O_4$ .—On heating furfural with potassium cyanide in presence of alcohol, a reddish crystalline mass is obtained, which can be purified by distillation in a current of carbonic acid, and crystallisation from toluene and alcohol. The compound obtained crystallises in delicate prisms (m. p.  $135^\circ$ ), sparingly soluble in hot water and ether, soluble in warm alcohol and toluene. It has feeble acid properties, dissolving in alkalis, with formation of an intensely dark-coloured liquid, which gives two remarkable absorption-bands, one between the lines C and D, the other between D and E.

It is probable that furoin, on reduction, yields a compound analogous to deoxybenzoin, but the author did not obtain it in a sufficiently pure state for analysis. Acetic anhydride converts furoin into *acetyl-furoin*,  $C_{10}H_7O_4.Ac$ , which crystallises in needles (m. p.  $76^\circ$ ), easily soluble in alcohol and ether, sparingly soluble in water.

*Furil*,  $C_{10}H_6O$ , corresponding to benzil, is obtained by dissolving furoin in the least possible quantity of soda, and passing through the solution a rapid stream of air; the furil separates out in delicate needles, which may be washed with water and crystallised from

alcohol. Furil forms golden-yellow needles (m. p.  $162^{\circ}$ ), sparingly soluble in cold alcohol and ether, easily soluble in water. On oxidising an acid solution of furil by dry air, it is converted into furilic acid, of probable composition  $C(OH)(C_4H_3O)_2.COOH$ . This compound is sparingly soluble in alcohol and ether, very unstable in the moist state, and decomposes entirely when heated to  $100^{\circ}$ . With bromine, furil gives an addition-product, *furil octobromide*,  $C_{10}H_6O_4Br_8$ , which forms golden horny crystals, melting at  $185^{\circ}$  and decomposing into dibromo- and monobromo-furil. The former,  $C_{10}H_4Br_2O_4$ , crystallises in golden-yellow leaflets (m. p.  $185^{\circ}$ ), insoluble in water, but dissolving in alkalis with formation of salts of *dibromofurilic acid*. The barium salt,  $(C_{10}H_5Br_2O_3)_2Ba$ , crystallises in delicate white needles. The *monobromofuril* crystallises in golden-yellow leaflets, and resembles the dibromo-compound in its chemical properties.

*Benzofuroin*,  $C_{12}H_{10}O_3$ .—A compound intermediate between benzoin and furoin is prepared by heating a mixture of benzaldehyde, furfural, and potassium cyanide in presence of alcohol; the crude product of the reaction is purified by crystallisation from benzene and alcohol. Benzofuroin crystallises in delicate prisms (m. p.  $137-139^{\circ}$ ), soluble in hot alcohol and benzene, sparingly soluble in water. In its properties it is intermediate between benzoin and furoin; its composition may be expressed by the formula  $CHPh(OH).CO.C_4H_3O$ , or  $Ph.CO.CH(OH).C_4H_3O$ . The author considers it probable that both of the isomerides are formed together, which would account for the want of uniformity of melting point of various preparations; but no separation into two definite compounds could be effected. Benzofuroin behaves towards oxidising agents in various ways. In alkaline solution, it is oxidised by air into benzoic acid; with dilute nitric or chromic acids, it yields benzaldehyde; and by feebly alkaline Fehling solution, it is converted into *benzofuril*,  $C_{12}H_8O_3$ . This compound crystallises in golden-yellow needles (m. p.  $41^{\circ}$ ), soluble in alkalis, with formation of *benzofurilic acid*; with bromine it gives *benzofuril tetrabromide*,  $C_{12}H_4O_3Br_4$ , crystallising in delicate golden needles; it melts at  $128^{\circ}$  with slight decomposition, which becomes violent at  $160^{\circ}$ . Benzofurilic acid,  $C_{12}H_{10}O_4$ , crystallises in short transparent prisms (m. p.  $108^{\circ}$ ), easily soluble in alcohol or ether. With concentrated sulphuric acid, benzofurilic, like benzoic acid, gives remarkable colour reactions; it dissolves in cold sulphuric acid, with formation of a blood-red colour; but if sulphuric acid is poured into an ethereal solution of the acid, a red-violet solution is produced, which rapidly changes to a blue-violet tint. V. H. V.

**Hexmethyltrimethylenediamine Bromide.** By C. F. ROTH (*Ber.*, 14, 1351).—This compound is obtained by heating trimethylene bromide at  $100^{\circ}$  for six hours with aqueous trimethylamine, as a crystalline mass, easily soluble in water, very sparingly in cold, more readily in hot alcohol. By crystallisation from hot alcohol, it is obtained in fine, colourless, slightly hygroscopic needles, having the composition  $Me_6(CH_2)_3N_2Br_2 + H_2O$ , and giving off their water at  $100^{\circ}$ . It differs in constitution from Hofmann's trimethylbromethylium bromide by containing 2 mols. trimethylamine to 1 mol.

bromide, whereas Hofmann's compound contains only one; and this difference of constitution is shown by a corresponding difference in the reaction of the two compounds with silver nitrate, hexmethyltrimethylenediamine bromide, when boiled therewith in aqueous solution, giving up all its bromine, whereas Hofmann's compound gives up only half. On agitating the bromide in aqueous solution with silver chloride, the bromine is easily replaced by chlorine, and the solution of the resulting chloride yields with platinic chloride a very sparingly soluble platinochloride, having the composition  $\text{Me}_6(\text{CH}_2)_3\text{N}_2\text{Cl}_2, \text{PtCl}_4$ .

By the action of trimethylene bromide on triethylamine, a similar addition-product is obtained, respecting which the author promises a further communication.  
H. W.

**Two New Derivatives of Thiocarbamide.** By M. NENCKI and N. SIEBER (*J. pr. Chem.* [2], **25**, 72—81).—Thiocarbamide dissolves in ethyl acetoacetate, and on adding water, a crystalline precipitate is obtained, having the formula  $\text{C}_5\text{H}_6\text{ON}_2\text{S}$ . This substance is sparingly soluble in cold water, alcohol, and ether, more readily in hot water. It dissolves readily in alkalis, and on adding an acid, is reprecipitated in pale yellow rhombic prisms. It melts above  $300^\circ$ , and is not desulphurised by iodine, metallic oxides, &c. Silver nitrate added to its hot aqueous solution gives an amorphous yellow precipitate of  $\text{C}_5\text{H}_4\text{Ag}_2\text{N}_2\text{SO}$ . The authors consider this substance to be the thiocarbamide of methylacetylenecarboxylic acid,  $\text{CMe} : \text{C.CO.S.C}(\text{NH}_2) : \text{NH}$ . The yield is small.

**Thiouvinuric Acid**,  $\text{C}_4\text{H}_4\text{N}_2\text{SO}_2$ .—This acid is obtained, as hydrobromide, by heating concentrated aqueous solutions of thiocarbamide and dibromoracemic acid on the water-bath, sulphur separating. The pure acid forms colourless oblique rhombic tables or needles, of the formula  $\text{C}_4\text{H}_4\text{N}_2\text{SO}_2 + 2\text{H}_2\text{O}$ . It is sparingly soluble in cold water, more readily in hot water, and but slightly in alcohol or ether. It reduces alkaline solution of cupric oxide in the cold, cuprous oxide being precipitated; with hot concentrated solutions a mirror of metallic copper is deposited. It gives a deep violet coloration with ferric chloride, resists the action of most desulphurising agents, but is decomposed on long boiling with concentrated alkalis. It unites with both acids and bases, forming crystalline salts. The calcium salt,  $(\text{C}_4\text{H}_3\text{N}_2\text{SO}_2)_2\text{Ca}$ , crystallises in rhombic plates; the magnesium salt,  $(\text{C}_4\text{H}_3\text{N}_2\text{SO}_2)_2\text{Mg}$ , in indistinct plates; the zinc salt,  $(\text{C}_4\text{H}_3\text{N}_2\text{SO}_2)_2\text{Zn}$ , is precipitated in microscopic concentrically grouped needles on mixing hot aqueous solutions of zinc acetate and thiouvinuric acid; the hydrobromide,  $\text{C}_4\text{H}_4\text{N}_2\text{O}_2\text{HBr}$ , and hydrochloride, are both anhydrous; the nitrate,  $\text{C}_4\text{H}_4\text{N}_2\text{SO}_2\text{HNO}_3 + \text{H}_2\text{O}$ , crystallises in long white needles. The authors suggest the constitution  $\text{CH.CO.CO.S.C}(\text{NH}_2) : \text{NH}$  for thiouvinuric acid. Dibromsuccinic acid, when heated with thiocarbamide, yields fumaric acid.

A. J. G.

**Action of Hydrogen Dioxide on Aromatic Compounds.** By A. R. LEEDS (*Ber.*, **14**, 1382—1384).—The author has already shown that benzene, subjected to the action of hydrogen dioxide, is gradually

converted into phenol, with simultaneous formation of oxalic acid and a small quantity of a yellow substance (Abstr., 1881, 719). Phenol itself is but very slightly attacked by hydrogen dioxide at ordinary temperatures, but on boiling it is converted into a varnish-like substance. *Naphthalene*, digested with hydrogen dioxide, yields a small quantity of naphthol, which is not further attacked by the dioxide, even in large excess; at the boiling heat, however, a varnish is produced. On adding hydrogen dioxide to a solution of *anthracene* in glacial acetic acid, a precipitate is formed, which, when treated with an excess of the dioxide, is slowly converted into anthraquinone. *Benzenesulphonic acid* is but very slightly attacked by the dioxide, merely assuming a brown colour, after several hours' boiling. These results show that hydrogen dioxide acts on organic bodies, often by substitution of OH for H, sometimes by oxidation, or in both ways simultaneously.

*Diphenylamine*, *Dimethylaniline*, *Xylidine*, *Naphthylamine*, and *o-Toluidine*, in the form of acetates, or dissolved in glacial acetic acid, and treated with successive portions of a 1·2 per cent. solution of the dioxide, rise of temperature being avoided, yielded coloured liquids and solid products, the composition of which was not ascertained.

*Aniline* and *p-Toluidine* behaved differently, the solutions of their acetates in hydrogen dioxide depositing, on gentle heating, brownish crystalline precipitates, while, at higher temperatures, varnish-like substances were formed. The crystalline precipitates were purified from small quantities of the varnishes by sublimation at a very gentle heat. The sublimate obtained from paratoluidine formed yellow needles, and after repeated crystallisation from alcohol, splendid orange-coloured needles, melting at 143—144°, and giving by analysis numbers agreeing with the formula of azotoluene,  $C_{14}H_{14}N_2$ . The same compound was obtained in small quantity by Barsilowsky (Abstr., 1881, 432) by the action of a very dilute solution of potassium permanganate on toluidine sulphate, and in large quantity by treating the same salt with potassium ferrocyanide and hydroxide.

Aniline, treated in like manner with hydrogen dioxide, is converted into azobenzene, in broad red crystals melting at 66°. H. W.

**Action of Benzyl Chloride on Diphenylamine.** By R. MELDOLA (*Ber.*, 14, 1385—1386).—The direct product of this reaction is a thick glutinous oil which, when exposed to the air, gradually turns green—a change which may be more quickly effected by the use of more powerful oxidising agents, the best result being obtained with a mixture of arsenic and hydrochloric acids. The green dye-stuff thus produced was exhibited at the International Exhibition in Paris in 1878, under the name of "Viridine." Under certain circumstances, as, for example, when a mixture of diphenylamine and benzyl chloride in molecular proportions is heated for some hours in the water-bath in contact with aqueous soda-ley, the chief product is *benzylidiphenylamine* (m. p. 87°), the compound which Bernthsen and Trompeter obtained by reduction of benzenediphenylthiamide,  $C_6H_5.CSN(C_6H_5)_2$ . The green dye obtained by the author does not appear, however, to be a direct derivative of benzylidiphenylamine.

To prepare viridine, diphenylamine is boiled in a flask with reversed



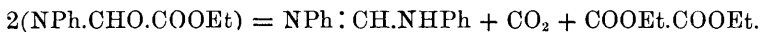
condenser for some hours—as long, indeed, as hydrochloric acid continues to escape—with twice the quantity of benzyl chloride required by the equation,  $\text{NHPh}_2 + \text{C}_7\text{H}_7\text{Cl} = \text{NC}_7\text{H}_7\text{Ph}_2 + \text{HCl}$ . The excess of benzyl chloride is then distilled off, and the remaining thick oil is heated for several hours on the water-bath with hydrochloric and arsenic acids, whereby a thick green melt is obtained, which, after careful washing with water and cooling, forms a brittle mass; and, on pulverising this mass, drying it, and repeatedly extracting it with cold benzene or toluene, the hydrochloride of the new base remains in the form of a bronze-coloured powder. To purify this hydrochloride, it is converted into the base by treating it with alcohol, benzene, and caustic alkali; and, on adding water to the solution of the bases in benzene, it separates as a layer of dark red-brown oil. The watery layer is then removed, and gaseous hydrogen chloride passed into the benzene solution, whereupon the hydrochloride separates in the form of a bronze-coloured micro-crystalline powder.

The new green is distinguished by the facility with which it forms a sulphonic acid. On stirring up the hydrochloride with sulphuric acid, a sulphonic acid is immediately formed, insoluble in water, but easily soluble in caustic alkalis. In this state it dyes wool or silk exactly in the same manner as "Nicholson's Blue." It is known in commerce as "Alkali-green." When the solution in sulphuric acid is raised to a higher temperature, sulphonic acids are formed, which are soluble in water.

Similar dye-stuffs are obtained by the oxidation of products resulting from the action of benzyl chloride on methyldiphenylamine,  $\beta$ -naphtholdiphenylamine, &c. The action of benzyl chloride on other monamines, primary, secondary, and tertiary, *e.g.*, aniline and its homologues, dimethylaniline, &c., likewise gives rise to oily products convertible into dye-stuffs by oxidation.

H. W.

**A New Method of Preparing Methenyldiphenylamidine.** By E. LELLMANN (*Ber.*, 14, 2512—2513).—With the object of making phenylurethanes in which the hydrogen of the amido-group should be replaced by an acid radical, the author tried the action of ethyl chloroformate on different anilides, and with acetanilide and benzanilide obtained no action. When, however, formanilide is mixed with an equivalent quantity of ethyl chloroformate, it dissolves, and after a short time gas is evolved and a crystalline magma separates. By dissolving the product in alcohol, treating it with soda, and purifying the precipitate by crystallising it from light petroleum, methyldiphenyldiamine is obtained in fine needles (m. p.  $137^\circ$ ). The author suggests the following as the possible course of the reaction; the desired urethane is formed thus:  $\text{NHPh}.\text{CHO} + \text{Cl}.\text{COOEt} = \text{NPh}.\text{CHO}.\text{COOEt} + \text{HCl}$ , but, being very unstable, breaks up further, thus:—

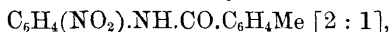


D. A. L.

**Anhydro.compounds.** By H. HÜBNER (*Annalen*, 210, 328—396).—This is a continuation of a former paper (comp. Abstr., 1881,

1130), and many of the compounds described in it have been subjects of short notices in the *Berichte*.

*Paratoluic Acid and Diamides*.—*Tolylorthonitranilide*,



is obtained from paratoluic chloride and orthonitraniline. It forms yellow prisms insoluble in water (m. p. 110°). By reduction it forms

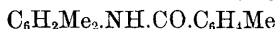
*anhydrotolylidiamidobenzene*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{C}.\text{C}_6\text{H}_4\text{Me}$  (Abstr., 1878,

144). The hydrochloride of this anhydro-base,  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{HCl}$ , the platinochloride, sulphate, and nitrate are described.

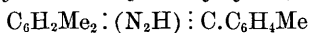
*Ditolylorthodiamidobenzene*,  $\text{C}_6\text{H}_4(\text{NH}.\text{CO}.\text{C}_6\text{H}_4\text{Me})_2$ , is formed, simultaneously with the anhydro-base, when prepared from paratoluic chloride and orthophenylenediamine; it is separated from the anhydro-base by its sparing solubility in glacial acetic acid. It forms colourless needles (m. p. 228°).

*Paratoluic Acid and Tolylenediamine*.—*Tolylenemetanitrotoluide*,  $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2).\text{NH}.\text{CO}.\text{C}_6\text{H}_4\text{Me}$  [1 : 3 : 4 (1 : 4)], is prepared from metanitroparatoluidine and paratoluic chloride; it crystallises from alcohol in golden-yellow needles, insoluble in water (m. p. 165–166°). On reduction with tin and hydrochloric acid, it yields *anhydrotolylidiamidotoluene*, already described in this Journal (*loc. cit.*). The hydrochloride and sulphate of this base are sparingly soluble salts; whereas the nitrate is easily soluble.

*Paratoluic Acid and Xylenamine*.—*Paratolylxylide*,



(m. p. 139°), is obtained from xylidine (b. p. 215–220°) and paratoluic chloride. It forms colourless needles, insoluble in water, but soluble in alcohol and glacial acetic acid. On treating the solution of this compound in glacial acetic acid with nitric acid, it yields *paratolylnitroxylide*,  $\text{C}_6\text{H}_2(\text{NO}_2)\text{Me}_2.\text{NH}.\text{CO}.\text{C}_6\text{H}_4\text{Me}$  (m. p. 187°), which crystallises from alcohol in yellow needles. On reduction this nitro-compound yields *anhydrodiamidoparatolylxylene*,



(m. p. 217°); it crystallises from alcohol in long colourless needles; it is sparingly soluble in water. Chromic acid oxidises this compound to an uncrystallisable acid. The salts of this base are crystalline and sparingly soluble in water; the formula of the hydrochloride is  $\text{C}_{16}\text{H}_{16}\text{N}_2.\text{HCl}$ .

*Amido-anhydro-compounds*.—Metanitrobenzoparatoluide, and the metanitrobenzometanitroparatoluide, obtained by nitrating the former, also the anhydro-base formed by reducing this latter compound, have already been described (Abstr., 1878, 144). The sulphate of the anhydro-base,  $\text{C}_{14}\text{H}_{13}\text{N}_3.\text{H}_2\text{SO}_4$ , is sparingly soluble in water, whilst the nitrate,  $\text{C}_{14}\text{H}_{13}\text{N}_3.\text{HNO}_3$ , is an easily soluble salt. Anhydrobenzamidotoluic acid, and the ketamine obtained from it, have been described in this Journal (Abstr., 1878, 503).

*Anhydrosalicyldiamidobenzene* is obtained from salicylorthonitranilide, as described in this Journal (Abstr., 1880, 556).

*Anhydro-bases and Iodine.*—*Anhydrobenzodiamidobenzene tri-iodide*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH}_2\text{I.I}_2 \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{CPh}$ , is obtained by heating an alcoholic solution of the

base with iodine. It crystallises in leaflets somewhat resembling iodine in colour, and having a green iridescence; is soluble in alcohol, but insoluble in the other oxidising solvents. When boiled with water it is resolved into iodine and the iodide of the anhydro-base.

*Monalkyl-compounds.*—The iodides of these bases are obtained by treating the anhydro-base with the iodides of the alcohol radicles, and from the iodide the free base is prepared. In this way *monamyl-anhydrobenzodiamidobenzene iodide*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N}:\text{CPh} \\ \diagup \quad \diagdown \\ \text{NHAmI} \end{smallmatrix}$ , has been prepared; it crystallises from aqueous solutions in light yellow needles. The hydrochloride,  $\text{C}_{18}\text{H}_{20}\text{N}_2\text{HCl}$ , and the sulphate have been prepared, and from the latter the free base or its hydroxide has been obtained by treatment with sodium carbonate.

In a similar manner *monethyl-anhydracetdiamidotoluene iodide*,  $\text{C}_{11}\text{H}_{14}\text{N}_2\text{HI} \cdot \text{H}_2\text{O}$  (m. p.  $141\cdot5$ — $143\cdot5^\circ$ ), has been prepared, and from it the ammonium base,  $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{N}:\text{CMe} \\ \diagup \quad \diagdown \\ \text{NHEt(OH)} \end{smallmatrix} + 2\text{H}_2\text{O}$ , which melts below  $30^\circ$ , and, when placed over sulphuric acid, loses water and forms the free base, which crystallises from alcohol in large colourless tablets, melting at  $93^\circ$ . The nitrate,  $\text{C}_{11}\text{H}_{14}\text{N}_2\text{HNO}_3$  (m. p.  $93^\circ$ ), is obtained by decomposing the iodide with silver nitrate; it crystallises from water in colourless needles, which are sparingly soluble in cold water.

II. *Dialkyl-compounds.*—The tri-iodides of these compounds are obtained by heating the anhydro-bases with the iodides of the alcohol radicles in sealed tubes at  $180$ — $210^\circ$ , and from the tri-iodide so obtained a series of compounds have been prepared similar to the *diethyl-* and *diamyl-anhydrobenzylidiamidobenzene-compounds*, described in this Journal (Abstr., 1879, 923).

*Dimethyl-anhydrobenzodiamidobenzene tri-iodide*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N}:\text{CPh} \\ \diagup \quad \diagdown \\ \text{NMe}_2\text{I}_3 \end{smallmatrix}$  (m. p.  $140\cdot5^\circ$ ), forms reddish-brown needles. The moniodide,  $\text{C}_{15}\text{H}_{15}\text{N}_2\text{I}$  (m. p.  $280^\circ$ ), crystallises from water in colourless needles. The hydroxide,  $\text{C}_{15}\text{H}_{15}\text{N}_2\text{OH}$ , is insoluble in water, but soluble in hot alcohol (m. p.  $152^\circ$ ). The sulphate, nitrate, and chloride of this base are easily soluble in water; the platinochloride,  $(\text{C}_{15}\text{H}_{15}\text{N}_2\text{Cl})_2\text{PtCl}_4$ , forms an orange-yellow crystalline precipitate.

The corresponding diethyl- and diamyl-compounds have been already described (*loc. cit.*).

Similar *dimethyl-* and *diethyl-*derivatives of *anhydrobenzodiamidotoluene* have also been prepared, as well as the *diethyl-*derivatives of *anhydracetdiamidotoluene*.

*Anhydro-compounds of Phenols.*—*Monobenzoparamidophenol*,



[1 : 4] (m. p.  $227\cdot5^\circ$ ), is obtained by the action of benzoic chloride on paramidophenol hydrochloride; it crystallises from glacial acetic acid

in colourless needles; sparingly soluble in the ordinary solvents, save glacial acetic acid.

*Paranitrophenol benzoate*,  $C_6H_4(NO_2).O\bar{B}z$  [4 : 1] (m. p.  $142^\circ$ ), prepared from paranitrophenol and benzoic chloride, is insoluble in water, but soluble in alcohol. When reduced with tin and hydrochloric acid it forms *paramidophenol benzoate* (m. p.  $153-154^\circ$ ), which crystallises from alcohol in hot glacial acetic acid in colourless leaflets. The properties of this compound show it to be isomeric with benzoyl paramidophenol.

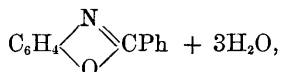
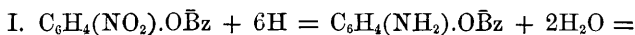
*Metanitrobenzoyl-paramidonitrophenol*,



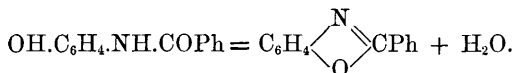
is obtained by the nitration of benzoyl-paramidophenol. It is sparingly soluble in glacial acetic acid, but easily soluble in aniline, from which it crystallises in yellow needles (m. p.  $225^\circ$ ). When boiled with sodium carbonate, it is resolved into metanitrobenzoic acid and paramidonitrophenol. This latter compound is sparingly soluble in water, but easily soluble in alcohol and ether, and crystallises in colourless needles, having the formula  $OH.C_6H_3(NH_2).NO_2 + H_2O$ , which, when heated, melt at  $180^\circ$ , and lose the molecule of water, forming yellow needles (m. p.  $206^\circ$ ). The potassium, sodium, and barium salts of this acid are described.

*Anhydrobenzamidophenol*,  $C_6H_4 \begin{array}{c} \diagup O \\ \diagdown N \end{array} = CPh$  (m. p.  $103^\circ$ ), which has

been described by Ladenburg (*Ber.*, 9, 1526), may be obtained by reducing orthonitrophenol benzoate, thus:—



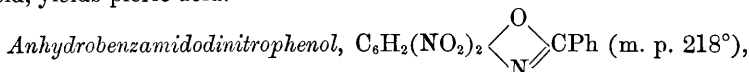
or by the action of heat upon benzorthamidophenol, thus:—



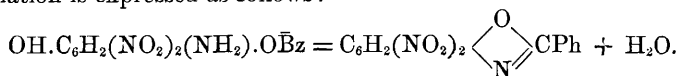
*Orthonitrophenol benzoate*,  $C_6H_4(NO_2).O\bar{B}z$  [2 : 1] (m. p.  $58^\circ$ ), is obtained from orthonitrophenol and benzoic chloride: it crystallises from petroleum in colourless, silky, lustrous prisms.

*Orthobenzamidophenol benzoate*,  $NH\bar{B}z.C_6H_4.O\bar{B}z$  [2 : 1] (m. p.  $176^\circ$ ), obtained from benzoic chloride and the amidophenol, is sparingly soluble in alcohol, insoluble in water, but soluble in glacial acetic acid and benzene. When boiled with barium carbonate suspended in water, it yields *orthobenzamidophenol*,  $OH.C_6H_4.NH\bar{B}z$ , and barium benzoate. *Orthobenzamidophenol* is insoluble in water, but soluble in alcohol, &c., and melts at  $167^\circ$ ; it forms no salts. When its solution in glacial acetic acid is poured into cold nitric acid, *benzamidodinitrophenol* is obtained, having the formula  $OH.C_6H_2(NO_2)_2.NH\bar{B}z$ , which crystallises from glacial acetic acid in greenish-yellow needles (m. p.  $220^\circ$ ). It readily forms metallic derivatives; those of potassium, ammonium,

barium, magnesium, zinc, and silver are described. By heating it with concentrated hydrochloric acid, it is resolved into benzoic acid and the known picramic acid (m. p. 167°). Its ethereal solution, treated with nitrogen trioxide, yields a diazo-compound,  $C_6H_2(NO_2)_2O.N_2$ , which, boiled with alcohol, forms *α*-dinitrophenol,  $C_6H_3(OH)(NO_2)_2$  [1 : 2 : 4] (m. p. 114°); it crystallises from alcohol in four-sided yellow tables. The above diazo-compound, when boiled with dilute sulphuric acid, yields picric acid.



is obtained by heating orthobenzamidodinitrophenol with phosphoric anhydride at 130°, also by the action of concentrated nitric acid on picramine benzoate, the nitric acid acting as a dehydrating agent. Its formation is expressed as follows:—



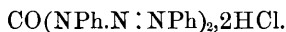
It forms small colourless leaflets, sparingly soluble in alcohol, but easily soluble in glacial acetic acid, chloroform, &c. Its production from picramic acid shows this latter compound to contain the “hydroxyl” and “amido” groups in the ortho-positions.

Picramine benzoate is obtained by the action of benzoic chloride on picramic acid; it forms colourless leaflets (m. p. 218—219°).

P. P. B.

**Action of Phosgene on Diazoamido-derivatives.** By A. SARAUW (*Ber.*, 14, 2442—2448).—This is an appendix to the work published by the author (*ibid.*, 2180) on the action of phosgene on methyldiphenylamine.

*Phosgene and Diazobenzanilide.*—On passing a current of the gas through diazobenzanilide (diazoamidobenzene) dissolved in benzene, there is a slight elevation of temperature, and a white crystalline precipitate (m. p. with decomposition 101°) is formed, insoluble in benzene and petroleum; it contains a large quantity of chlorine, and gives off hydrochloric acid over sulphuric acid in a vacuum. By warming with water, it is easily decomposed, with copious evolution of nitrogen and the formation of a small quantity of *amidoazobenzene* (m. p. 127°), besides *phenol* (b. p. 181—182°), and *carbanilide*, which emitted the odour of phenyl isocyanide on warming with phosphoric anhydride. The body itself is possibly *diphenyldiazobenzenecarbamide hydrochloride*—



In the same way phosgene reacts with diazobenzeneparatoluide (or *paradiazotolueneanilide*), yielding a white crystalline substance, possibly *diparatolyldiazobenzenecarbamide*,  $CO[NC_6H_4Me.N : NPh]_2$ , which, when decomposed with warm water, yields *phenol*, mixed with *cresol*, and *paraditolyldicarbamide*,  $CO(NH.C_7H_7)_2$ , (m. p. 256°).

D. A. L.

**Researches on Benzoyl Compounds.** By O. DÖBNER (*Annalen*, 210, 246—284).—The object of these researches (of which the greater

part has already appeared in various numbers of the *Berichte*) was to extend Zincke's reaction to the building up of bodies from acid chlorides and oxygenated and other derivatives of the aromatic hydrocarbons, by replacing the hydrogen of the hydroxyl and amido-groups by an acid radical, so that the remaining hydrogen of the hydrocarbon chain could come into play and react with the chloride of an acid radical.

*Benzophenol*,  $\text{COPh.C}_6\text{H}_4.\text{OH}$ .—Phenyl benzoate was heated with benzoic chloride and zinc chloride at  $180^\circ$ ; benzophenyl benzoate was first formed (m. p.  $112.5^\circ$ ), which, on saponification, yielded benzophenol (m. p.  $134^\circ$ ); by the action of acetic chloride, the acetate (m. p.  $81^\circ$ ) was obtained. On treatment with sodium-amalgam, benzophenol is converted into benzhydrylphenol,  $\text{CHPh(OH).C}_6\text{H}_4.\text{OH}$ , in fine needles (m. p.  $161^\circ$ ). On fusion with potash, benzophenol is decomposed into benzene and parahydroxybenzoic acid. An attempt to procure benzophenol from phenyl acetate was not successful, the acetyl being simply replaced by the benzoyl-group.

By the action of benzoic chloride on resorcinol, the dibenzoate is first formed, then a mixture of a benzoiresorcinol and dibenzoiresorcinol dibenzoate. After saponification, the two bodies are separated by alcohol, in which the benzoiresorcinol (m. p.  $144^\circ$ ) is easily, and the dibenzoiresorcinol (m. p.  $149^\circ$ ) is hardly soluble; the diacetate of the latter body melts at  $150^\circ$ .

With pyrocatechol the dibenzoate (m. p.  $84^\circ$ ) was obtained in like manner, and from this benzopyrocatechol (m. p.  $145^\circ$ ).

With quinol, dibenzoquinol (m. p.  $199^\circ$ ) is formed from the dibenzoate, and crystallises in golden-yellow needles, soluble in alkalis, with red colour.

Aniline was also subjected to the same reaction: in this case the two hydrogen-atoms of the amido-group had been replaced by phthalyl. By the action of benzoic chloride, phthalylbenzoanilide is obtained, which, on treatment with potash, is converted into benzoylaniline (m. p.  $124^\circ$ ), a basic body forming crystalline salts with acids. Treated with excess of methyl iodide, the methiodide of dimethylbenzoaniline is obtained. By the action of acetic chloride, acetobenzoylanilide is formed in long colourless needles (m. p.  $153^\circ$ ). In a similar manner, the benzoyl compound is obtained (m. p.  $152^\circ$ ). Benzophenylisonitril is formed when an alcoholic solution of benzoylaniline is heated with potash and chloroform; its vapour has the characteristic odour of isonitrils (m. p.  $118\text{--}119^\circ$ ).

Benzophenyl carbamate,  $\text{PhCO.C}_6\text{H}_4.\text{NH.COEt}$  (m. p.  $189^\circ$ ), and benzophenylthiocarbamide (m. p.  $166^\circ$ ) were obtained by the usual reactions, and crystallise in large brilliant plates.

By treatment with nitrous acid, benzoylaniline is converted into a benzophenol, identical with that obtained from phenol. Dehydrating agents convert it into benzophenylnitrile,  $\text{C}_6\text{H}_4\text{--}\angle\text{N}\text{--}\text{CPh}$ , (m. p.  $118^\circ$ ).

Benzoylbenzoic acid,  $\text{PhCO.C}_6\text{H}_4.\text{COOH}$ , is formed by the action of benzoic chloride on benzoic anhydride; it melts at  $160^\circ$ , and is soluble in hot water. When heated with soda-lime, it is split up into benzene and carbonic anhydride; fused with potash, it yields only benzoic acid;

it is identical with the metabenzoylbenzoic acid of Ador (*Ber.*, **13**, 320).

Like chlorine and nitric acid, benzoic chloride forms with phenol and aniline para-compounds, whilst a meta-compound is obtained from benzoic acid.

J. K. C.

**Resorcyanin.** By W. SCHMIDT (*J. pr. Chem.* [2], **25**, 81—83).—By heating resorcinol (1 part), ethyl acetoacetate (1 part), and zinc chloride (2 parts), for 15—20 minutes, a considerably larger yield of resorcyanin is obtained than by Wittenberg's method of heating resorcinol with zinc chloride and citric acid. By substituting sulphuric acid for zinc chloride, the reaction goes on still more readily.

A. J. G.

**Chlorine and Bromine Derivatives of Quinone.** By S. LEVY and G. SCHULTZ (*Annalen*, **210**, 133—164).—F. Wöhler (*Annalen*, **51**, 155) showed that by the action of concentrated hydrochloric acid on quinone, chloroquinol is produced; all attempts, however, to replace another atom of hydrogen in this manner failed. The reaction, according to Wichelhaus, consists firstly in the oxidation of the acid by the quinone and production of free chlorine, which then reacts on the quinol. On repeating the experiments with a view of obtaining further substitution, it was found that the chlorinated quinones gave the same reaction with hydrochloric acid that quinone does, although not quite so easily. The monochloroquinol was obtained by dissolving quinone in concentrated hydrochloric acid; it was then oxidised to monochloroquinone. The latter by further treatment with hydrochloric acid was converted into a dichloroquinol, which, on oxidation, gave the dichloroquinone produced by the action of chlorine on quinone. The constitution of this body, termed by the authors  $\alpha$ -dichloroquinone, was determined. On treating the  $\beta$ -dichloroquinone, obtained from trichlorophenol with hydrochloric acid, it yielded the same trichloroquinol as the  $\alpha$ -compound. By oxidation and further treatment with hydrochloric acid, tetrachloroquinone may be obtained.

*Monochloroquinol* is best prepared by passing a current of dry hydrochloric acid gas into a solution of quinone in chloroform; it forms colourless, transparent, monosymmetric crystals melting at  $106^\circ$ , and boiling with very slight decomposition at  $263^\circ$ , soluble in water, alcohol, and ether. When heated with phthalic anhydride and sulphuric acid it yields a chlorinated quinizarin. The *diacetyl*-compound, prepared in the usual way, melts at  $72^\circ$  and crystallises in prisms belonging to the asymmetric system. The *dibenzoyl*-compound melts at  $130^\circ$ . Attempts to introduce iodine, cyanogen, and fluorine into the quinone group in the same way as chlorine failed.

*Monochloroquinone* is obtained on adding potassium dichromate and sulphuric acid to an aqueous solution of the chloroquinol, the mixture being cooled by ice; a small quantity of dichloroquinone is formed at the same time. Monochloroquinone forms reddish rhombic crystals, melting at  $57^\circ$ , and agrees entirely in its properties with the quinone obtained by Theodor.

$\alpha$ -*Dichloroquinol*, prepared by the action of concentrated hydrochloric acid on the above, is obtained in long needles (m. p.  $166^\circ$ ).

Its *diacetyl*-compound crystallises in needles (m. p.  $141^{\circ}$ ) belonging to the monosymmetric system.

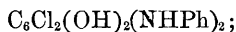
$\alpha$ -*Dichloroquinone*,  $C_6H_2O_2Cl_2$  [ $O : O : Cl : Cl = 1 : 4 : 2 : 5$ ], is easily obtained by adding a few drops of concentrated nitric acid to the aqueous solution of the corresponding quinol; it forms monosymmetric crystals, melting at  $159^{\circ}$ . That its constitution is that given above is proved by its formation from amidoparadichlorobenzene by oxidation.

By the further action of concentrated hydrochloric acid, *trichloroquinol* is formed; the *dibenzoyl*-compound of this body melts at  $174^{\circ}$ . Trichloroquinone is not soluble in concentrated hydrochloric acid, but on long boiling it is converted into flakes of *tetrachlorquinol*, which crystallise from its solution in benzol in monosymmetric prisms; its *dibenzoyl*-compound melts at  $233^{\circ}$ .

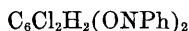
*Dibromoquinone*, obtained by the oxidation of tribromophenol with nitric acid, forms brilliant yellow plates, melting at  $122^{\circ}$ . On oxidation with chromic acid, tribromophenol yields bromanil.

*Monochloromonobromoquinone* is formed by heating monochloroquinone with concentrated hydrobromic acid; trichlorobromoquinol is also obtained in a similar way from trichloroquinone; it melts at  $229^{\circ}$ , and crystallises in the monosymmetric system. The quinone obtained by oxidation with nitric acid, forms yellow crystals, which sublime before melting, and are monosymmetric. J. K. C.

**Action of Ammonia and Ammonia Bases on Chlorinated Quinones.** By H. v. KNAPP and G. SCHULTZ (*Annalen*, **210**, 164—191).—After giving at some length a historical sketch of the discoveries and theories published with reference to ammoniated chloroquinones, the authors show that the theories of Hofmann and Wichelhaus with respect to the constitution of these bodies are most in accordance with known facts, and proceed to test the correctness of these views by an examination of the reduction-products of these bodies. Hofmann's formula for chloranilamide, for instance, is  $O_2 : C_6Cl_2(NHPh)_2$ , and this on reduction would yield—



whilst if chloranilamide were expressed by the formula—



(Wichelhaus), it would yield on reduction dichloroquinol and aniline or hydrazobenzene, or benzidine and  $\beta$ -diamidodiphenyl. The experiments made were found to confirm Hofmann's theory completely. The chlorinated quinones were obtained by the well known methods. With benzoquinone the reactions of ammonia and amines were only qualitatively studied; compounds were formed by ammonia, aniline, orthotoluidine, and monacetylbenzidine. By the action of orthotoluidine, a body was obtained in brownish-yellow crystals, soluble in alcohol, and in sulphuric acid with a red-violet colour; whilst the compound obtained from acetylbenzidine and quinone, gave a blue solution in sulphuric acid.

Trichloroquinone introduced into alcoholic ammonia dissolves,



forming a dark solution, from which a brown substance separates. On redissolving and treatment with a little caustic potash, it may be obtained in carmine-red needles; the yield was, however, too small for a systematic investigation of this substance. With aniline, trichloroquinone yields a body in thin plates, having the constitution of a monochlorodianilidoquinone, and converted by reduction with stannous chloride into the corresponding quinol, thus proving the correctness of Hofmann's theory. Compounds were also obtained with trichloroquinone and ortho- and para-toluidine and other amines, but were only examined qualitatively.

Chloranil, as was shown by Laurent (*Annalen*, **52**, 347), when treated with alcoholic ammonia, yields chloranilamide at first in brownish needles, which, on purification with weak potash, give a violet solution. A concentrated solution of stannous chloride in hydrochloric acid reduces it to dichlorodiamidoquinol, which is very soluble in water, and in this state is easily oxidised to the quinone. Both these bodies are strongly attacked by nitrous and nitric acids; chloropicrin, and in the latter case also oxalic acid being formed.

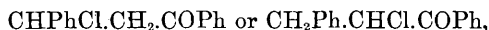
With aniline, chloranil is converted into dichlorodianilidoquinone, soluble in sulphuric acid with blue colour; on treatment with stannous chloride the corresponding quinol is formed, which is easily reoxidised to quinone by ferric chloride.

Trichlorotoluquinone appears to behave in the same way as its benzene homologue. Dichloronaphthaquinone gives copper-red needles of monochloroanilidonaphthaquinone (m. p.  $202^{\circ}$ ). On reduction with stannous chloride, the corresponding quinol is obtained in reddish crystals (m. p.  $170-171^{\circ}$ ). The diacetyl-compound of this quinol melts at  $168-169^{\circ}$ .  
J. K. C.

**Condensation of Ketones with Aldehydes.** By L. CLAISEN and A. CLAPARÈDE (*Ber.*, **14**, 2460—2068).—This paper is a continuation of a former communication (*Abstr.*, 1881, 422—423). *Dibenzylidene-acetone* or cinnamone,  $\text{CO}(\text{CH}:\text{CHPh})_2$ , is also obtained as a red-brown mass, when 40 parts glacial acetic and 30 parts sulphuric acid are dropped into a mixture of 20 parts benzaldehyde with 6 parts acetone, the whole being allowed to remain in the cold, and after 6—8 hours poured into iced water; it is purified by washing with soda-solution, and recrystallising from boiling ether. Small quantities are formed when a mixture of benzaldehyde and acetone is digested for some time with dilute soda-solution, and further the body obtained by Schmidt (*Abstr.*, 1881, 889) is this substance. The crystals are monoclinic (measured by Bodewig). *Dibenzylidene-acetone* is decomposed when heated, yielding a distillate having the odour of a hydrocarbon. On adding bromine to the chloroform solution of the ketone, a precipitate is obtained consisting of small white needles (m. p.  $206-208^{\circ}$ ) of dibenzylidene-acetone tetrabromide,  $\text{C}_{17}\text{H}_{14}\text{OBr}_4$ , sparingly soluble in chloroform and alcohol. *Benzylidene acetone*,  $\text{CHPh}:\text{CH}.\text{COMe}$ , is best prepared when a mixture of benzaldehyde and acetone in molecular proportions with double this proportion of acetic anhydride and a little zinc chloride is heated for 8—10 hours in a steam-bath. The product is then washed with

water, the portion boiling below  $200^{\circ}$  distilled off, and the residue distilled in a vacuum. It forms a pale yellow pleasant-smelling thick oil, which will remain fluid for a long time if a trace of impurity is present, but if pure, solidifies to a beautiful, almost colourless, crystalline mass of very brilliant thick tables (m. p.  $41-42^{\circ}$ , b. p.  $260-262^{\circ}$ , thermometer entirely in vapour). It is easily soluble in alcohol, ether, benzene, and chloroform, still more so in warm petroleum, from which it separates partly as an oil and partly crystalline. Its solution in sulphuric acid is of the same orange-red colour as the dibenzylidene-acetone, and the colour disappears on the addition of water. By treating the solution with 1 mol. bromine, a *dibromide*,  $C_{10}H_{10}OBr_2$ , is formed, soluble in chloroform and in hot alcohol, from which solution it crystallises in short colourless needles (m. p.  $124-125^{\circ}$ , but soon after decomposes, turning brown and giving off gas). This body is identical with Engler and Leist's acetocinnamone obtained by distilling cinnamic acid with calcium acetate (*Ber.*, **6**, 255), the difference in properties being due to impurity.

A mixture of acetophenone and benzaldehyde in molecular proportions, when saturated with hydrochloric acid gas in the cold, solidifies in about 12 hours to a compact yellow-brown crystalline mass (leaflets). After a few days, it is heated on a water-bath, left to solidify, and then dissolved in petroleum. *Benzylidene phenyl ketone*,  $CHPh:CH.COPh$ , crystallises out on cooling in long broad pale-yellow transparent prisms, or when the solution is slowly evaporated in well-formed thick hexagonal tables (m. p.  $57-58^{\circ}$ , rhombic, measured by Lehmann); on keeping, they gradually become dim and opaque without altering. It boils at  $345-348^{\circ}$  (uncorr.), and distils without decomposition. Chloroform, ether, carbon bisulphide, and benzene dissolve it easily, cold alcohol only slightly, and petroleum very sparingly. It can also be prepared by the method described above with sulphuric acid, the mixture of benzaldehyde and acetophenone being diluted with glacial acetic acid; it is likewise formed by heating the mixture for some time with acetic anhydride at  $160-170^{\circ}$ . The *dibromide*,  $C_{15}H_{12}OBr_2$ , forms colourless short prisms (m. p.  $156-157^{\circ}$ ), easily soluble in hot and sparingly in cold alcohol. The hydrochloric acid compound—



is prepared as above described, the crystalline mass being dissolved directly in boiling alcohol; on cooling, it sets to a crystalline magma of white leaflets of the compound. It crystallises from ether in colourless rhombic leaflets, which, when heated quickly, melt at  $119-120^{\circ}$ , and when slowly heated, at  $110-112^{\circ}$ ; at this point it gives off hydrochloric acid, and changes to non-chlorinated ketone. It is very sparingly soluble in cold, somewhat more so in boiling alcohol and ether. By oxidation with dilute nitric acid, benzylidene phenyl ketone yields benzoic and benzoylformic acids. When heated with hydrochloric acid (sp. gr. 1.12) for some hours at  $180-200^{\circ}$ , it breaks up into benzaldehyde and acetophenone, and with hydriodic acid and amorphous phosphorus it forms dibenzylmethane (b. p.  $290-295^{\circ}$ ), and a small quantity of an oil of high boiling point. With hydrochloric acid

gas, acetone and aldehyde give mixed products, with acetone and chloral anhydride no change takes place, acetone and salicylic anhydride yield resinous and uninviting bodies, and acetone and furfuraldehyde also no condensation-products.

D. A. L.

**Action of Acetone on Furfuraldehyde and on Benzaldehyde in the Presence of Alkaline Solutions.** By L. CLAISEN (*Ber.*, **14**, 2468—2471).—The results of the experiments obtained with benzaldehyde and acetone (p. 1511), support the conclusion that the residual aldehyde groups, *i.e.*, aldehydes from which the atom of oxygen has been removed, can combine only with those methyl- (and probably also methylene-) groups that are directly connected with carbonyl. Schmidt's results (*Abstr.*, 1881, 889) point to quite another conclusion, but as his bodies have some very surprising properties, for example, the body  $C_{21}H_{20}O_6$  has the low b. p.  $229^\circ$ , whilst it has been shown that the bodies  $C_{10}H_{10}O$  and  $C_{15}H_{12}O$  boil respectively at  $261^\circ$  and  $345^\circ$ , the author has repeated the experiments with the following results:—

*Action of Dilute Soda-solution on a Mixture of Acetone and Furfuraldehyde.*—The furfuraldehyde, acetone, water, and dilute soda solution were mixed in the proportions given by Schmidt, and after remaining 24 hours at the ordinary temperature, during which time an oil separated out, the product was exhausted with ether, the ether distilled off, and the thick yellow liquid residue fractionally distilled under reduced pressure. An oil passed over boiling constantly at  $135-137^\circ$  under 33—34 mm. pressure; the brown very viscid residue after some time solidified to a radiating crystalline mass, consisting partially of difurfurylideneacetone. The distillate gave numbers (carbon differing 2.5 per cent. from Schmidt's) for the formula  $C_8H_8O_2$ , which is *monofurfurylidene acetone*,  $C_4H_3O.CH:CH.COME$ ; it soon solidifies to a compact prismatic crystalline mass (m. p.  $39-40^\circ$ ), which gradually turns brown in the air, and then has a much stronger odour of furfuraldehyde than the freshly prepared substance. It dissolves easily in alcohol, ether, and chloroform, but less easily in light petroleum, from which it is deposited in colourless crystals. It dissolves in acetic (or benzoic) chloride with a pale red colour, which changes to green slowly or quickly when warmed, and disappears on adding water. With sulphuric acid, traces of the substance give rise to a yellowish-brown coloration, which turns to a deep dark wine-red on applying heat.

In the same manner the analogous experiment with benzaldehyde produced *dibenzylidene acetone*,  $C_{17}H_{14}O$ , and in larger quantities *monobenzylidene acetone*. The latter by the further action of benzaldehyde and dilute soda (to 7 parts of substance dissolved in 150 parts alcohol and 200 parts of water, 5 parts of benzaldehyde, and 20 parts 10 per cent. soda solution) is easily converted into the dibenzylidene-derivative. By replacing the benzaldehyde in this experiment by furfuraldehyde, *benzylidene furfurylidene ketone* is obtained. It will be seen, therefore, that the action of alkalis on mixtures of acetone and aldehydes is analogous to that of other condensation agents.

D. A. L.

**Benzoic Bromide.** By L. CLAISEN (*Ber.*, **14**, 2473—2476).—There being no efficient method for preparing this body, the author has adopted the following:—Finely powdered (fused) benzoic acid (3 mols.) and phosphorus tribromide (2 mols.) are warmed and digested together in a flask with reflex condenser; after a quarter of an hour's heating the mixture is distilled in a vacuum, and the distillate rectified at ordinary pressure. From 500 grams of benzoic acid, 400 grams of bromide are obtained. Benzoic bromide is a colourless pungent liquid (b. p. 218—219°, thermometer entirely in vapour, and sp. gr. 1.5700 at 15°). On cooling it to -24°, it solidifies to a white prismatic compact crystalline mass (m. p. about 0°). In its behaviour, it resembles benzoic chloride, but is more easily decomposed.

"Benzoic bromide," prepared by Liebig and Wöhler's method by the action of bromine on benzaldehyde, or by Paternò's method with bromine and ethyl benzoate, is not this body, but a compound of the formula  $\text{CHPhBr} \cdot \text{BzO}$ , *benzylidene bromobenzoate*. The author has prepared some of it by mixing equivalent quantities of benzaldehyde and benzoic bromide in a stoppered bottle; the temperature soon rises to 40°, and after some days the whole solidifies. Recrystallised from boiling light petroleum, it forms thick short tabular prisms (m. p. 69—70°), soluble in ether, alcohol, glacial acetic acid, and chloroform: it is unstable, and in the air soon becomes dull, begins to fume and to smell of benzaldehyde and benzoic bromide, whilst the melting point rises to 120°. Even in the desiccator, it rapidly undergoes decomposition, and can only be preserved under petroleum in a good stoppered bottle. By distillation, it is broken up into its components, which after some time again unite to form the double compound.

Benzoic bromide seems to combine easily with aldehydes and ketones, especially with acetone, for as soon as the two are mixed they solidify to a crystalline mass. An attempt to combine the bromide with unsaturated hydrocarbon-compounds gave negative results.

D. A. L.

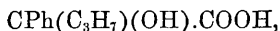
**Aromatic Substances in the Animal Body.** By E. BAUMANN (*Zeits. Phys. Chem.*, **4**, 304—322).—The author believes the hydroparacoumaric acid obtained by the putrefaction of tyrosine to be identical with that already known. Its alkaline, barium, and calcium salts are readily soluble in water. The zinc salt is nearly insoluble, and is precipitated in the crystalline form on adding zinc sulphate to a solution of the ammonium salt. The copper compound is also nearly insoluble; both bodies contain 2 mols. of water of crystallisation. The author was successful in obtaining the acid in the crystalline form from half a litre of fresh pus. Parahydroxyphenylacetic acid was obtained from 240 litres of human urine, but only traces of hydroparacoumaric acid.

The decomposition-products of hydroparacoumaric acid were found to be parahydroxyphenylacetic acid, phenol, and paracresol.

By fusing tyrosine with potash, parahydroxybenzoic acid alone was obtained.

W. N.

**Aromatic Hydroxy- and Amido-acids.** By J. PLÖSCHL (*Ber.*, **14**, 1316).—*Cuminglycollic* or *phenylpropylglycollic acid*,



which Raab obtained, with some difficulty, by treating cumene with hydrocyanic and hydrochloric acid, is more readily prepared by adding fuming hydrochloric acid, with constant stirring, to an ice-cold ethereal solution of cumic aldehyde mixed with pulverised potassium cyanide, decanting the ethereal solution of the resulting cyanhydrin; and, after the ether has evaporated, pouring the remaining oil into fuming hydrochloric acid, which dissolves it, and leaving the solution for a day or two in a moderately warm place. It then becomes quite solid, from separation of sal-ammoniac and the acid formed by the reaction; and on diluting with water and distilling with steam, the impurities of the cumic aldehyde (cumic acid and cymene) pass over, while the cuminglycollic acid remains in the retort, together with a little resin, and separates in large quantity on cooling. It may be purified by dissolving it in sodium carbonate, evaporating to dryness, and exhausting the residue with cold water, whereupon nearly all the resin is left behind, and the pure acid may be separated by supersaturation with hydrochloric acid. Cuminglycollic acid melts at  $158^\circ$ , dissolves readily in alcohol and ether, less easily in water.

*Cuminamidacetic acid*,  $\text{C}_{10}\text{H}_{12}(\text{NH}_2).\text{COOH}$ , the analogue of the preceding acid, is prepared by treating the corresponding hydramide with hydrocyanic acid, decomposing the resulting di-imidonitril with hydrochloric acid and water—whereby cumic aldehyde and cumamidonitril are obtained—and converting the latter into the amido-acid. Cuminamidacetic acid melts, with decomposition, at  $197^\circ$ , dissolves sparingly in cold, more freely in hot water, but is insoluble in alcohol and in ether. It unites with 1 mol. hydrochloric acid, and forms a crystallised copper salt.

*Salicylglycollic acid*,  $\text{OH}.\text{CHPh}.\text{COOH}$ , is prepared from salicylaldehyde in a similar manner, but with certain modifications, for which the original paper must be consulted. It may be extracted from the aqueous solution by ether, and remains, even after prolonged sojourn over sulphuric acid, in the form of a syrup. On redissolving it in water and agitating with animal charcoal, it is obtained in the form of a strongly acid, pale sulphur-yellow solution, which, when saturated with carbonate of calcium or zinc, forms easily soluble crystallisable salts. If the original aqueous solution of the acid be not completely exhausted with ether, it leaves on evaporation, together with sal-ammoniac, a brown oil, which on drying solidifies to a crystalline cake consisting of salicylglycollic anhydride,  $\text{C}_6\text{H}_4.\text{CH}(\text{OH}).\text{COO}$ .

H. W.

**Azophthalic Acid.** By A. CLAUS and O. MAY (*Ber.*, **14**, 1330—1333).—To prepare this acid, sodium-amalgam from 60 g. sodium and 4 kg. mercury is gradually added with brisk agitation to a cooled and slightly alkaline solution of nitrophthalic acid in dilute soda-ley, and after the whole has been added, the liquid, which has assumed a

red-brown colour, is warmed for some time on the water-bath till bubbles of hydrogen begin to escape. The solution concentrated to a syrup and left at rest, deposits the sodium azophthalate in fine crystals, easily purified by repeated crystallisation from a small quantity of water. The free acid is obtained by treating the sodium salt with hydrochloric, sulphuric acid, &c., in the form of a loose golden-yellow precipitate, which in this form is moderately soluble in water. When dry, it forms a fine powder of pure yellow colour, soluble in a large quantity of boiling water, from which the acid is deposited on slow cooling, partly in small needle-shaped crystals. Its aqueous solutions have a strongly acid reaction. In ether and alcohol it is not more soluble than in water. When heated, it turns brown at about  $220^{\circ}$ , begins to melt at  $230^{\circ}$ , and melts completely, with rapid decomposition, at  $250^{\circ}$ . By very cautiously heating small quantities of the dry acid to  $140$ — $150^{\circ}$ , a sublimate is obtained, having the form of yellowish-white slender needles. *Sodium azophthalate*,  $C_{16}H_6N_2O_8Na_4 + 10H_2O$ , forms large yellowish-red crystals, which appear to be combinations of two monoclinic prisms, and exhibit a strong dichroism; they effloresce at ordinary temperature, and give off all their water at  $110^{\circ}$ . The anhydrous salt is very hygroscopic; the crystallised salt is extremely soluble in water. The *potassium salt*,  $C_{16}H_6N_2O_8K_4 + 6H_2O$ , crystallises in long slender needles, mostly united in dense tufts, having a brown colour and splendid metallic lustre; they deliquesce in moist air, and give off all their water at  $110^{\circ}$ . Acid azophthalates of the alkali-metals have hitherto been obtained only in small crystals of uncertain composition. The *normal ammonium salt*, obtained by repeated addition of ammonia to an evaporating solution of the acid in excess of ammonia, is a brown resinous mass. The *silver salt* is obtained as a yellow pulverulent anhydrous precipitate, insoluble in water, not much altered by light, detonating slightly when heated. The *magnesium salt*,  $C_{16}H_6N_2O_8Mg_2 + 18H_2O$ , crystallises readily in groups of large yellowish-red crystals, permanent in the air, moderately soluble in water. The *barium salt* is a yellowish pulverulent anhydrous precipitate, insoluble in water.

By dry distillation of a mixture of calcium azophthalate with lime, azophenylene is obtained, together with a number of other products, mostly of oily consistence. By heating with tin and hydrochloric acid or with stannous chloride, azophthalic acid is easily converted into a new acid, probably benzidine-tetracarboxylic acid.

H. W.

**Azobenzenesulphonic Acids.** By H. LIMPRICHT (*Ber.*, 14, 1356—1359).—Two of these acids ( $\alpha$  and  $\beta$ ) are obtained by gradually adding azobenzene to 5—8 pts. fuming sulphuric acid, heated in an oil-bath to  $130^{\circ}$ , continuing the heating at  $150$ — $170^{\circ}$  for about two hours—avoiding evolution of sulphurous anhydride—and pouring the thick oily mass into water. The liquid is then neutralised with slaked lime, strained and evaporated; the calcium salt which separates is converted into potassium salt, and the latter is resolved by repeated crystallisation into the salts of the two isomeric acids. The properties of these acids and their salts are as follows:—

$\alpha$ .

$C_{12}H_8N_2(SO_3H)_2 \cdot 2H_2O$  (dried over oil of vitriol). Concentric groups of red deliquescent needles.

$C_{12}H_8N_2(SO_3K)_2 \cdot 2\frac{1}{2}H_2O$  (air-dry). Rather large red prisms, often concentrically grouped or united in crusts. Easily soluble in hot, sparingly soluble in cold water.

$C_{12}H_8N_2(SO_3)_2Ba$  (anhydr.) Crystalline precipitate, or from dilute solution, rosettes of microscopic needles; nearly insoluble in water.

$C_{12}H_8N_2(SO_3)_2Ca$  (anhydr.) Crystalline, yellow-red precipitate; slowly separating in crusts from hot solution.

$C_{12}H_8N_2(SO_3)_2Pb \cdot H_2O$ , or anhydr. Precipitate crystallising from hot water, in warty groups of small deep red prisms.

$C_{12}H_8N_2(SO_3)_2Cu \cdot 6H_2O$ . Rosettes of brown crystalline laminæ; sparingly soluble in cold, easily in hot water.

$C_{12}H_8N_2(SO_3Ag)_2$  (anhydr.) Precipitate, crystallising from hot water in crusts of dark red nodules.

*Chloride*,  $C_{12}H_8N_2(SO_2Cl)_2$ . Crystallises from hot ether or benzene, in short broad, brown-red needles; m. p. 220—222°.

*Amide*,  $C_{12}H_8N_2(SO_2NH_2)_2$ . Obtained by prolonged heating of the chloride with ammonia. Thin, reddish-yellow laminæ or needles, dissolving with difficulty in hot water, with moderate facility in boiling alcohol, and not melting at 300°.

 $\beta$ .

Obtained from the Ag salt by precipitation with HCl, or from the chloride by heating with water. Uncrystallisable syrup.

$C_{12}H_8N_2(SO_3K)_2 \cdot 2\frac{1}{2}H_2O$ . Deep yellow needles, dissolving in water in all proportions; must therefore be recrystallised from alcohol.

Yellow needles; very soluble in hot, somewhat less in cold water.

Crusts of indistinct crystals; very soluble in water, less soluble in alcohol.

From concentrated solution of the potassium salt with lead nitrate, as a yellow crystalline precipitate; easily soluble in hot, less in cold water.

$C_{12}H_8N_2(SO_3Ag)_2 \cdot H_2O$  (?) Yellow precipitate, crystallising from hot water in yellow laminæ; easily soluble in hot, less in cold water.

Crystallises from benzene in hard warty crystals; from alcohol or ether in slender red needles; m. p. 123—125°.

Sparingly soluble in water, more freely in alcohol, and crystallises from the latter in slender yellowish needles, often grouped in tufts; m. p. 258°.

$\alpha$ -Hydrazobenzenesulphonic acid,  $C_{12}H_{10}N_2(SO_3H)_2 \cdot 2H_2O$  (?). A hot concentrated solution of potassium azobenzenesulphonate, mixed with stannous chloride, deposits this acid on cooling in white crystals; and on evaporating the mother-liquor, coloured crystals of the same acid are obtained, which may be purified by crystallisation from hot water,

with addition of animal charcoal. The pure crystals are transparent, colourless, highly lustrous tablets, sparingly soluble in cold, more readily in hot water; nearly insoluble in alcohol. They effloresce on exposure to the air, become coloured at  $200^{\circ}$ , and carbonise without tumefaction at a higher temperature.

The following salts have been examined:  $C_{12}H_{10}N_2(SO_3K)_2 \cdot 3H_2O$ . Colourless, silky, efflorescent needles.— $C_{12}H_{10}N_2(SO_3)_2Ba \cdot H_2O$ . Colourless, shining, brittle, efflorescent needles, easily soluble in hot water.— $C_{12}H_{10}N_2(SO_3)_2Pb$  (anhydr.). Tufts of yellowish needles, sparingly soluble in cold, more freely in hot water. A *silver salt* is obtained by decomposing the ammonium salt with silver nitrate, as a white crystalline precipitate, decomposed by hot water.

When the hydrazo-acid is suspended in ice-cold water through which a stream of nitrous gas is passed, it assumes a brownish colour, and after pressing between filter-paper, detonates when heated, and gives off nitrogen when boiled with water.

$\beta$ -Hydrazobenzenesulphonic acid does not appear to be formed by the action of stannous chloride on the potassium salt of the  $\beta$ -azo-acid.  
H. W.

**Acid Produced by the Action of Hydrogen Bromide on the Diazo-derivative of Hydrazobenzenesulphonic Acid.** By H. LIMPRICHT (*Ber.*, 14, 1359—1361).—The hydrazobenzenesulphonic acid,  $SO_3H \cdot C_6H_4 \cdot NH \cdot NH \cdot C_6H_4 \cdot SO_3H$ , described by Mahrenholz, Gilbert, and Brunnemann (*Abstr.*, 1880, 805—808), yields, when treated with nitrous acid, a diazo-compound,  $C_{12}H_{10}N_4S_2O_8$ , which is converted by heating with water into a phenolsulphonic acid:  $C_{12}H_{10}N_2S_2O_8 + H_2O = 2[C_6H_4(OH) \cdot SO_3H] + 2N_2 + O$ , and by heating with highly concentrated hydrobromic acid into an acid having the composition of a bromobenzenesulphonic acid,



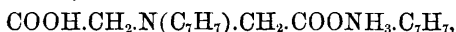
The diazo-compound must be added by small portions, and the liquid then gently heated, whereupon it gives off nitrogen, becomes deep red, and leaves on evaporation a dark-coloured residue, which is to be dissolved in water, neutralised with lead carbonate, and mixed with alcohol, to remove bromide of lead. The acid separated from the lead salt by hydrogen sulphide has not been obtained in crystals; neither do any of its salts appear to crystallise. The *barium salt*,  $(C_6H_4Br \cdot SO_3)_2Ba$ , obtained by neutralisation, and freed from an admixed resinous body by treatment with alcohol, dries up to a gummy, faintly yellowish mass, easily soluble in water and in alcohol. The *potassium salt*,  $C_6H_4Br \cdot SO_3K$ , obtained by decomposing the barium salt with potassium carbonate, is a gummy mass, easily soluble in water, insoluble in absolute alcohol. The *chloride* is a white mass, hard in the cold, softening when warmed, melting at  $185$ — $187^{\circ}$ . The *amide* forms tufts of needles, melting and decomposing at  $225$ — $230^{\circ}$ .

H. W.

**Formation of Substituted Imidodiglycollic Acids in the Preparation of Paratolyl- and Phenyl-glycine.** By P. J. MEYER



(*Ber.*, **14**, 1323—1326).—*Para*-tolyl-glycine and *Para*-tolyl-imidodiglycollic acid. *Para*-tolyl-glycine, which Schwebel first obtained by the action of monochloroacetic acid on *para*-toluidine in ethereal solution (*Abstr.*, 1878, 302), is best prepared by introducing the two substances into water, without addition of ether, and applying heat for a while. The end of the reaction is indicated by the production of large quantities of toluidine hydrochloride, and the cooled solution quickly deposits nearly the whole of the tolyl-glycine in crystals, while the filtrate, after standing for some hours, yields another body, also observed by Schwebel, who regarded it as *ortho*-tolyl-glycine, attributing its formation to the presence of *ortho*-toluidine in the commercial toluidine which he used. This body crystallises in small shining needles and laminæ; dissolves readily in water, alcohol, and acids; reduces silver salts immediately with aid of heat, slowly in the cold; and gives with very dilute solutions of cupric sulphate the emerald-green coloration characteristic of tolyl- and phenyl-glycine; but its melting point lies between 118° and 119° (116°—118°, Schwebel), differing, therefore, considerably from that of *ortho*-tolylglycine, which, according to Staats (*Abstr.*, 1880, 387) melts at 150°. It is decomposed by bases, with separation of *para*-toluidine, but on carefully neutralising the alkaline liquid, the original body is reproduced. These reactions show that the body in question is a salt of *para*-toluidine, isomeric or polymeric with tolyl-glycine, in fact, the primary tolyl-ammonium salt of *para*-tolyl-imidodiglycollic acid,



a composition which has been confirmed by the analyses of the corresponding copper and silver salts. Its occurrence, together with tolyl-glycine, is precisely analogous to that of imidodiglycollic acid, together with glycine, observed by Heintz (*Annalen*, **122**, 257 and 269) in the action of aqueous ammonia on monochloroacetic acid.

*Cupric Tollyl-imidodiglycollate*.— $\text{C}_7\text{H}_7 < \begin{smallmatrix} \text{CH}_2 \cdot \text{COO} \\ \text{CH}_2 \cdot \text{COO} \end{smallmatrix} > \text{Cu}$ , obtained by adding the toluidine salt to a hot concentrated solution of cupric sulphate, crystallises in small green needles, very slightly soluble in hot alcohol. A compound of *silver para*-tolyl-imidodiglycollate with *nitric acid*,  $\text{C}_7\text{H}_7\text{N}(\text{CH}_2 \cdot \text{COOAg})_2 \cdot \text{HNO}_3$ , is obtained by dissolving the toluidine salt in a small quantity of ammonia, filtering from separated toluidine, and mixing the filtrate with silver nitrate. It dissolves easily in excess of ammonia, blackens slowly at ordinary temperatures, but is immediately decomposed when heated.

*Phenylglycine and Phenylamidodiglycollic Acid*.—The phenylammonium salt of this acid,  $\text{COOH} \cdot \text{CH}_2 \cdot \text{NPh} \cdot \text{CH}_2 \cdot \text{COONH}_3\text{Ph}$ , is prepared, similarly to the tolyl-ammonium salt above described, by adding 2 mols. aniline and 1 mol. chloroacetic acid to hot water, and boiling for some time; but the preparation is more difficult, on account of its greater solubility; but by fractional crystallisation of the still warm solutions, and repeated fractionation of the later-separating and lower-melting crystallisations, the phenylammonium salt is at length obtained in white needles, having a faint yellowish tinge, and melting at 90°. Like the toluidine compounds, it dissolves in acids, yields

aniline when treated with bases, and likewise metallic salts, which, however, have not been analysed. The presence of this body, together with phenyl-glycine, may perhaps explain the difference between the melting point of the latter, as given by Michaelson and Lippmann (110°), and by the author (126—127°; this Journal, 1876, 1, 372).

H. W.

**Synthesis of Atrolactic Acid from Acetophenone.** By A. SPIEGEL (*Ber.*, 14, 1352—1355).—A mixture of acetophenone and its cyanhydrin,  $\text{CH}_3\text{C}(\text{OH})\text{Ph}.\text{CN}$ , dissolves in hydrochloric acid saturated at 0°, yielding probably in the first instance the corresponding amide, and afterwards atrolactic acid,  $\text{C}_9\text{H}_{10}\text{O}_3$ , which therefore, has the constitution  $\text{CH}_3\text{C}(\text{OH})\text{Ph}.\text{COOH}$ . The cyanhydrin of acetophenone is therefore identical with the nitril of atrolactic acid. This acid, after crystallisation from water, with the aid of animal charcoal, forms limpid spiculæ or scales, which become dull when left over sulphuric acid, and give off  $\frac{1}{2}$  mol. water of crystallisation at 80—85°. The acid dried over sulphuric acid melts at 89—91°; that dried at 80—85° melts at 93—94°.

Atrolactic acid or its nitril, heated at 130° with hydrochloric acid saturated at 0°, is converted into chlorhydratropic acid,



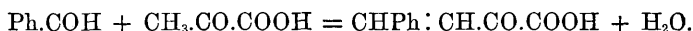
which when heated with caustic soda-solution, yields tropic acid, isomeric with atrolactic acid, and represented by the formula



H. W.

### **New Method for the Preparation of Cinnamylformic Acid.**

By L. CLAISEN and A. CLAPARÈDE (*Ber.*, 14, 2472—2473).—A mixture of molecular proportions of benzaldehyde and pyruvic acid is saturated in the cold with hydrochloric acid gas, the reaction which takes place being as follows:—



After some days, the brown viscid product is treated with ice-cold water, and the acid brought into solution by adding sodium carbonate; the solution is quite clear, but, on standing, a yellow gelatinous precipitate forms and is filtered off; it is insoluble in ether and alkaline carbonates. The filtrate is extracted with ether to remove unattacked benzaldehyde, and then treated with hydrochloric acid, by which means the acid separates as a pale yellow oil; this is dissolved in ether, dried with calcium chloride, and the ethereal solution evaporated in a desiccator. *Cinnamylformic acid*,  $\text{CHPh}:\text{CH}.\text{CO}.\text{COOH}$ , is a pale yellowish gummy mass, only slightly soluble in water; almost all the salts of this acid, with the exception of the alkali salts, are sparingly soluble or insoluble. With a solution of the ammonium salt, barium and calcium chlorides give white precipitates, which dissolve gradually on boiling; lead, a white; copper sulphate, a blue-green; ferric chloride, a pale brownish-yellow precipitate. The silver salt is but sparingly soluble even in boiling water. The acid itself is not very stable. The solutions of the salts become turbid even in the cold, and emit an odour of benzaldehyde.

D. A. L.

**New Method of Preparing Diphenylene and an Isomeride of the Same.** By H. STRASSER and G. SCHULTZ (*Annalen*, **210**, 191—195).—Paradiphenylcarboxylic acid, when treated with fuming nitric acid, is for the most part converted into dinitrodiphenylcarboxylic acid [ $\text{NO}_2 : \text{COOH} : \text{NO}_2 = 2 : 4 : 4$ ]. It may be purified by solution in hot alcohol, from which it separates in needles (m. p.  $252^\circ$ ); it is soluble in ether and in glacial acetic acid. The alkaline salts are easily soluble; the barium salt less so. The methyl salt, prepared in the usual way, crystallises easily in long needles (m. p.  $156^\circ$ ). On reduction with stannous chloride, it gives the diamido-acid, and this, when distilled with lime, yields  $\beta$ -diamidodiphenyl, part of which was converted into the corresponding  $\delta$ -diphenol for identification.

By the action of concentrated nitric acid on diparabromodiphenyl (m. p.  $164^\circ$ ) a dinitro-compound is formed, which, on reduction with stannous chloride, is converted into diamidodibromodiphenyl. Sodium amalgam replaces the bromine-atoms by hydrogen, and an isomeride of diphenylene and benzidine is formed as a yellow oil, which boils above  $360^\circ$ . Its basic and neutral salts are very soluble; with chlorine-water the solution of the hydrochloride gives a dirty green, and with bromine-water a white precipitate. The base is probably diortho-amidodiphenyl.  
J. K. C.

**Tolane Di-iodide.** By E. FISCHER (*Annalen*, **211**, 293).—On heating a mixture of tolane and iodine a violent reaction takes place, and the fused mass solidifies in crystals, which are washed with chloroform to remove the iodine and unattacked tolane.

Tolane di-iodide crystallises in colourless needles, sparingly soluble in alcohol, more readily in chloroform. When heated, it is completely decomposed into tolane and iodine, the vapours of which partially recombine on condensation. Alcoholic ammonia reconverts the di-iodide into the original hydrocarbon.  
V. H. V.

**Formation and Constitution of  $\beta$ -Naphthaquinone and some of its Derivatives.** By C. LIEBERMANN and P. JACOBSEN (*Annalen*, **211**, 36—84).—A considerable portion of this research has already appeared in the *Berichte* (**14**, 803, 1310, 1791), and in this volume (204, also Abstracts, 1881, 736).  $\beta$ -Naphthaquinone, obtained from  $\beta$ -naphthylamine, does not melt at  $110^\circ$ , but begins to blacken between  $115^\circ$  and  $120^\circ$ . It is identical with the  $\beta$ -naphthaquinone described by Stenhouse and Groves (*Annalen*, **189**, 153).

*Amido- $\beta$ -naphthol* is most conveniently prepared from  $\beta$ -naphthol-orange, the sodium salt of the benzenesulphonic acid of azo- $\beta$ -naphthol,  $\text{SO}_3\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_6(\text{OH})\beta$ . Sufficient hydrochloric acid is added to  $\beta$ -naphthol-orange, mixed with three times its weight of stannous chloride, to produce a crystalline magma. The mixture is stirred and heated until it becomes colourless; it is then collected on a funnel. The residue is dissolved in hot water and treated with sulphuretted hydrogen to remove the tin. On cooling, the filtrate from the sulphide of tin deposits a mixture of sulphanilic acid and amido- $\beta$ -naphthol hydrochloride. A second crop of crystals may be obtained by concentrating the filtrate, but these crystals contain a larger

quantity of sulphanilic acid, and cannot be advantageously employed in the preparation of  $\beta$ -naphthol. In order to separate the  $\beta$ -amidonaphthol from sulphanilic acid, the crystals are treated with an excess of sodium carbonate solution, and the liquid is repeatedly extracted with ether to dissolve out the amidonaphthol. The extract is distilled and the residue rapidly pressed between bibulous paper, in order to prevent oxidation. Amido- $\beta$ -naphthol is sparingly soluble in boiling water. It dissolves in ammonia, yielding a yellow solution which turns brown on exposure to the air.

The  $\beta$ -naphthaquinone obtained from amido- $\beta$ -naphthol by the method of Groves and Stenhouse, is identical with  $\beta$ -naphthaquinone from nitro- $\beta$ -acetonaphthalide and from nitro- $\beta$ -naphthol.

The preparation of  $\alpha$ -naphthaquinone from  $\alpha$ -naphthol-orange has been previously described (*Ber.*, **14**, 1315; and this volume, 203).

$\beta$ -Naphthaquinoneanilide,  $C_{10}H_{15}(O)(NPh)OH$ , is deposited when aniline ( $1\frac{1}{2}$  parts) is added to an alcoholic solution of  $\beta$ -naphthaquinone (1 part). It is insoluble in water, but can be recrystallised from boiling alcohol or glacial acetic acid. The anilide forms red needles, having a golden or green metallic lustre; it does not melt at  $240^\circ$ . The anilide is soluble in strong sulphuric acid and in solutions of alkalis; it is reprecipitated on neutralising the solvents.  $\beta$ -Naphthaquinoneparatoluide resembles the preceding compound by its solubility in cold potash-lye and reprecipitation from the alkaline solution on the addition of an acid. When these are acted on by glacial acetic acid at  $150^\circ$ , the anilide or toluidide of  $\alpha$ -naphthaquinone is produced (see also Zincke, *Ber.*, **14**, 1493). The explanation of this reaction is that the  $\beta$ -naphthaquinoneanilide is decomposed, yielding hydroxynaphthaquinone, which immediately acts on the aniline acetate, forming  $\alpha$ -naphthaquinoneanilide.

The authors have previously shown (*Ber.*, **14**, 1791, and this volume, 204) that the two oxygen-atoms in  $\beta$ -naphthaquinone occupy the ortho- $\alpha$ - $\beta$ -position in the same benzene nucleus.  $\beta$ -Naphthaquinone resembles phenanthraquinone in constitution.  $\beta$ -Naphthaquinone-

anilide and toluidide have the constitution  $NR.OH.O$  1 : 3 : 4, and the isomerides derived from  $\alpha$ -naphthaquinone have the constitution

$O.NR.H.O$  1 : 3 : 4.

W. C. W.

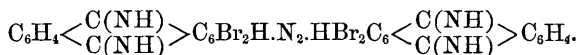
**Nitrobromanthraquinones.** By A. CLAUS and C. DIERNFELLNER (*Ber.*, **14**, 1333—1338).—The experiments recorded in this paper, which are a continuation of those of Claus and Hertel already described (*Abstr.*, 1881, 737), were made chiefly with the view of obtaining substitution-derivatives of anthraquinone, in which the bromine-atoms or nitro-groups may be accessible to simple transformation with potash, ammonia, &c., similar to that which is known to take place in the dinitrochlorobenzenes.

Dinitrobromanthraquinone,  $C_{14}H_5Br(NO_2)_2O_2$ , is formed by the action of fuming sulphuric acid (2 parts), and fuming nitric acid (3 parts) on tribromanthraquinone, at first in the cold, afterwards at boiling heat, and separates, on pouring the cooled liquid into water, as a

yellow bulky precipitate, which, after repeated crystallisation from glacial acetic acid, forms needle-shaped crystals having a fine yellow colour, and melting constantly at  $213^{\circ}$ . It dissolves also with moderate facility in benzene and chloroform, less readily in ether and in alcohol. It is not sublimable, but decomposes when heated above  $213^{\circ}$ , leaving a large quantity of nitrogenous charcoal. The alcoholic solution, treated with sodium-amalgam, gives a very fine and characteristic quinone reaction. Potash, ammonia, and aniline act on the compound with moderate facility, forming red products which have not yet been examined.

*Mononitrodibromanthraquinone*,  $C_{14}H_5Br_2(NO_2)O_2$ , is prepared by boiling tetrabromanthracene with nitric acid, not till the whole is dissolved, but for a short time only, then filtering the solution through glass-wool and pouring the filtrate into cold water. It is sublimable, and may thus be obtained in slender yellow needles, melting at  $245^{\circ}$ , soluble in glacial acetic acid, slightly soluble in alcohol, ether, and chloroform. By treatment with alcohol and sodium-amalgam, it is reduced in the same manner as nitroanthraquinone, yielding *amidanthraquinone*,  $C_{14}H_7(NH_2)O_2$  (m. p.  $154^{\circ}$ ), the reduction of the nitro-group and the replacement of the bromine by hydrogen taking place readily even at ordinary temperatures. By reduction with zinc and acetic acid, or with tin and hydrochloric acid, on the other hand, only the nitro-group is replaced, the product consisting of *amidodibromanthraquinone*,  $C_{14}H_5Br_2(NH_2)O_2$ , which by sublimation may be obtained in slender needles, having a fine red colour and melting at  $169-170^{\circ}$ . This compound dissolves but sparingly in all solvents, most readily in a mixture of alcohol and ether, not at all in dilute acids, and therefore has no basic properties. By sodium-amalgam, it is readily converted into amidoanthraquinone.

When nitrodibromanthraquinone is heated for some time with alcoholic ammonia in a sealed tube at  $100^{\circ}$ , a compound is obtained which partly separates in brown well-defined crystals, partly remains in the alcoholic liquid, and may be precipitated therefrom by water in brown flocks. This body has the composition  $C_{14}H_7Br_2N_2$ , and may be regarded as *tetrabromotetrimidazoanthracene*,



It dissolves with some difficulty in alcohol and ether, more readily in glacial acetic acid and benzene, forming orange-red solutions, and sublimes in beautiful light red needles which melt at  $233^{\circ}$ ; it is insoluble in water, alkalis, and dilute acids, even at the boiling heat.

*Dinitrodibromanthraquinone*,  $C_{14}H_4Br_2(NO_2)_2O_2$ , is prepared by boiling 1 part of tetrabromanthracene with 10 parts of a mixture of 2 parts fuming sulphuric and 3 parts fuming nitric acid till the whole is dissolved, pouring the product into cold water, and purifying it by recrystallisation from glacial acetic acid till it melts at  $239^{\circ}$ . It is very slightly soluble in alcohol and ether, somewhat more freely in benzene and chloroform, and crystallises from glacial acetic acid in small yellow needles. It is not sublimable, but is completely decomposed, with carbonisation, when heated above  $250^{\circ}$ .

With sodium-amalgam and alcohol, it gives the characteristic anthraquinone reaction, and by prolonged treatment therewith is completely converted into diamidanthraquinone (m. p. 236°). By treatment with tin and hydrochloric acid, the nitro-groups—or at least one of them—are easily reduced, but the bromine is not replaced by hydrogen. The product is a brown-red body crystallising from glacial acetic acid in compact groups of small red needles, melting at 180—183°, but not sublimable. It appears to consist of *nitramidodibromanthraquinone* or a mixture thereof with other products of reduction; at all events, it is converted by sodium-amalgam into diamidanthraquinone.

Dinitrodibromanthraquinone is readily attacked by alkalis, even in cold aqueous solution, with production of a red to brown liquid; when boiled with dilute alcoholic ammonia, it likewise yields a red compound, together with ammonium bromide. On heating a dilute faintly yellow alcoholic solution of dinitrodibromanthraquinone with aniline, the liquid assumes a fine purple-red colour, and on addition of water yields a dark violet precipitate, which dissolves with moderate facility in alcohol, ether, benzene, and glacial acetic acid, with production of extremely beautiful colours. H. W.

**Oil of Wild Thyme.** By P. FEBVE (*Compt. rend.*, **92**, 1290—1291).—This oil does not appear to have been examined before. A preliminary distillation separated the liquid into two products—one colourless, boiling at 170—200°, the other, strongly coloured, boiling between 200—250°. The first liquid was fractionated over sodium, and obtained of tolerably constant boiling point, 175—177°. It is a colourless liquid, with an odour of lemons, having a density of 0.873 at 0°, and a very feeble rotatory power. The density of its vapour, determined at 192.5° under 748 mm. pressure, was 4.78. The theoretical density of the hydrocarbon,  $C_{10}H_{14}$ , is 4.63, with which formula the percentage composition also agreed.

Ordinary sulphuric acid had no action upon it, but the Nordhausen acid dissolved it without elevation of temperature, and without disengagement of sulphurous anhydride; the resulting liquid was red, and entirely soluble in water.

From the foregoing, there can be no doubt that the liquid is a cymene,  $C_{10}H_{14}$ , containing probably some traces of a camphene hydrocarbon, to which perhaps its feeble rotatory power is due.

The higher boiling portions consisted chiefly of an oxidised body, which was isolated by dissolving it in solution of caustic soda and decanting the insoluble hydrocarbons. The phenol was then separated by treatment with dilute hydrochloric acid and shaking with ether; after several rectifications, it furnished a product boiling regularly at 233—235°.

It is a colourless oily liquid with a pungent odour recalling that of the original oil. Its density at 0° was 0.988, but it does not solidify in a mixture of ice and salt; however, the analysis corresponded well with the formula  $C_{10}H_{14}O$ , which shows it to be a thymol.

Treated with acetic chloride, it gives the acetic salt of thymol, which is a colourless liquid of pleasant odour, boiling at 244—245°.

J. W.

**Essential Oil of the Fruit of "Coriandrum sativum."** By B. GROSSER (*Ber.*, **14**, 2485—2508).—The oil used had sp. gr. 0.8719 at 15°, refractive index = 1.464; at 15°, with Wild's polaristrobometer,  $[\alpha]_D = -92.55$ ; another sample, sp. gr. 0.8720, gave  $[\alpha]_D = -88.4$ . Analysis led to the formula  $C_{10}H_{16}O$ . When fractionally distilled, the portion which passes over at 150—170° is turbid from the presence of water, but above this temperature the distillate is clear. Analysis of fraction 165—170° gave numbers for  $C_{20}H_{34}O$ ; and of fraction 190—196° gave the same results as the original oil. Both the oil and fraction 190—196° dissolve completely in cold alcoholic sulphuric acid (90 per cent. alcohol, 2 parts; sulphuric acid, sp. gr. 1.840, 1 part), a property also evinced by the monohydrate of lœvortatory turpentine oil (Flawitzky, *Ber.*, **12**, 2354). The fraction 165—170° also dissolves to a clear solution, but soon becomes turbid from separation of a terpene. A mixture of  $C_{10}H_{16}O$  and  $C_{10}H_{16}$ , never dissolves to a clear solution; the fraction 165—170° is therefore not a mixture of these bodies, but a definite compound, for, by repeated distillation, it boiled between 168—170°; its formation is thus explained,  $2C_{10}H_{16}O = C_{20}H_{34}O + H_2O$ . By distillation with phosphoric anhydride, oil of coriander yields a terpene, water being eliminated (Kawaler); the same change takes place when the oil is heated alone in a sealed tube at 200° for some time. Sodium acts on the oil, hydrogen being evolved, and the body  $C_{10}H_{17}ONa$  being formed; on decomposing this with dilute hydrochloric acid, instead of getting back  $C_{10}H_{16}O$ , the body  $C_{20}H_{34}O$  (b. p. 168—170°) is obtained. By conducting the experiment with sodium at 150—170° and decomposing the product with hydrochloric acid, the terpene,  $C_{10}H_{16}$  (b. p. 178—180°), is formed. By digesting the oil with acetic acid at 150—180° in a sealed tube, a body of the formula  $C_{28}H_{44}O$  is produced; with acetic anhydride, however, an acetate is formed,  $C_{10}H_{17}.AcO$ . Dry hydrochloric acid gas is absorbed by coriander oil with great avidity, water being formed: the oil,  $C_{10}H_{17}Cl$ , produced is of a feeble yellowish colour; has a neutral reaction, and a not unpleasant camphor-like odour; its sp. gr. = 0.9527 at 15°; when heated it decomposes, giving off hydrochloric acid. The absorption of hydriodic acid gas is very violent, often explosive, and the product explodes violently when warmed, even below 100°; the iodine estimation agrees with the formula  $C_{10}H_{17}I$ . These experiments tend to show that coriander oil has a hydroxyl-group, and its formula is therefore  $C_{10}H_{17}.OH$ . The iodide,  $C_{10}H_{17}I$ , gradually undergoes decomposition, and, by carefully heating it, after decomposition has set in, to about 140°, iodine and hydriodic acid are evolved, and, after about half an hour, the reaction is complete; *cymene* was recognised amongst other products.

Oxidation experiments with nitric acid were useless, for with strong acid the action is too violent, and with dilute acid there is no action at all.

With alkaline potassium permanganate the oxidation takes place in stages, according to the strength and quantity employed. With a concentrated solution of permanganate the action is extremely violent; with a more dilute solution the reaction is steadier, and the products are *acetic* and *oxalic acids* and *carbonic anhydride*. By adding a 1 per cent. solution of the permanganate to the oil, at the same time cool-

ing, until all the oil has disappeared from the surface, filtering off the manganese hydrate, and separating from the *potassium carbonate* by crystallisation and extraction with alcohol, a product is obtained which shows no tendency to crystallise. This product is treated with phosphoric acid and distilled with steam. The only volatile acid present is *acetic*. From the residue an acid,  $C_6H_{10}O_4$ , is separated, which does not crystallise, or form crystalline salts; it forms precipitates, however, with basic lead acetate and iron chloride, and may, therefore, possibly be *dimethyl-succinic acid*. If, however, dilute permanganate is used in quantity insufficient for complete oxidation, the product consists of a ketone,  $C_8H_{13}.COMe$ , which is a yellowish oil (sp. gr. 0.8970: b. p. 185—186°); does not solidify, even at  $-37^\circ$ ; is volatile with steam, and forms a crystalline compound with hydrogen sodium sulphite which melts when touched with the finger, and chars when heated. Oxidised with potassium permanganate, it yields the acid  $C_6H_{10}O_4$ , acetic acid, and carbonic anhydride, and finally, by further oxidation, oxalic acid.

D. A. L.

**Combination of Camphor with Aldehyde.** By P. CAZENÈVE (*Bull. Soc. Chim.* [2], **36**, 650—652).—When camphor is agitated with an aqueous solution of aldehyde, it unites with the latter, forming a liquid which floats on the top of the water. This compound, like that formed by camphor and hydrocyanic acid, dissociates at ordinary temperatures, leaving a residue of camphor. Its composition is not definite, but varies with the relative proportions of the two substances and with the temperature and pressure. Unlike the compound with hydrocyanic acid, it is decomposed by pure water, but, if the water contains a certain amount of aldehyde, decomposition does not take place. This relation between the *affinity of solution* and *affinity of combination* has already been observed in the case of the molecular combination of camphor with chloral hydrate. An aqueous solution of acetone forms no similar compound with camphor.

C. H. B.

**Properties of the Bromine-atoms in Mono- and Di-bromocamphor.** By R. SCHIFF (*Ber.*, **14**, 1377—1379).—In a former paper (Abstr., 1880, 892) the author showed that monobromocamphor is converted by nascent hydrogen and by alcoholic potash into camphor, and that bromonitrocarnphor is converted by these reagents into nitrocamphor. To these results must be added that dibromocamphor is converted by the same reagents, first into monobromocamphor, and then into camphor. The above-mentioned reactions of monobromocamphor are sufficiently explained, on the supposition that this compound contains the group  $OBr$ ; but with regard to dibromocamphor, the case is somewhat different, for the two bromine-atoms exhibit exactly similar reactions, and nevertheless there is only one atom of oxygen present. The author is, however, of opinion that all the reactions of bromocamphor warrant the assumption that it contains the group  $OBr$ , to which there must correspond a hydroxyl-group in camphor itself. The absence of phenolic properties in camphor need not be regarded as an objection to this view, when it is remembered that camphor does not contain an intact benzene-nucleus, but rather ap-



proximates to the types of saturated compounds. The formation of the dichloride by the action of  $\text{PCl}_5$  also becomes intelligible, bearing in mind that both camphor and the terpenes easily absorb hydrogen

chloride. A body of the formula  $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{C.OH} \\ \parallel \\ \text{CH} \end{smallmatrix}$ , when subjected to the

action of  $\text{PCl}_5$ , will first exchange its hydroxyl for chlorine; but the hydrogen chloride liberated at the same time will be immediately added to the molecule, forming the dichloride  $\text{C}_{10}\text{H}_{16}\text{Cl}_2$ . Monobromocamphor and phosphorus pentachloride do not act on one another even at  $100^\circ$ , a result which might be expected from the formula

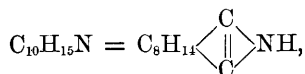
$\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{C.OBr} \\ \parallel \\ \text{CH} \end{smallmatrix}$ , whereas nitrocamphor,  $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{C.OH} \\ \parallel \\ \text{C.NO}_2 \end{smallmatrix}$ , is instantly at-

tacked by phosphorus pentachloride, with violent evolution of hydrochloric acid.

Dibromocamphor is stated in all manuals, on the authority of Swarts, to melt at  $114.5^\circ$ . By Montgolfier, however (*Bull. Soc. Chim.*, **23**, 253), it is said to melt at  $57^\circ$ ; and this result has been confirmed by Schiff.

H. W.

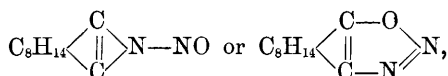
**Camphor-derivatives containing Nitrogen.** By R. SCHIFF (*Ber.*, **14**, 1375—1377).—The author showed, two years ago, that when an acidulated solution of amidocamphor is distilled in a stream of hydrogen, there is obtained, together with a yellow substance,  $\text{C}_{20}\text{H}_{31}.\text{NO}_2$ , a base represented either by the formula—



or by  $\text{C}_{10}\text{H}_{17}\text{NO} = \text{C}_8\text{H}_{14}\begin{smallmatrix} \text{C-OH} \\ \parallel \\ \text{C-NH}_2 \end{smallmatrix}$  (Abstr., 1880, 892). The second

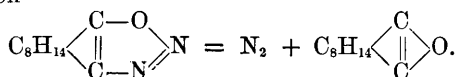
formula is empirically the same as that of amidocamphor, but the author does not regard the body in question as identical with ordinary amidocamphor.

When the hydrochloric acid solution of amidocamphor is distilled in a stream of hydrogen till the distillates pass over colourless, and the remaining solution is evaporated to dryness, the hydrochloride of this base is obtained; and on dissolving this salt in 90—100 parts of ice-cold water, adding a dilute ice-cold solution of potassium nitrite in slight excess, and then acetic acid, there separates out on the surface of the liquid a yellow body which crystallises from ether in large yellow tablets, melting, without decomposition, at  $73\text{--}74^\circ$ . This body has the composition  $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}$ , and might be represented by either of the two constitutional formulæ—



accordingly as it is deduced from one or the other formula of the

base. Experiment shows, however, that it is not a nitroso-compound, but a true diazo-compound represented by the second formula. By reduction with zinc-dust and acetic acid it yields, not a secondary hydrazine-base, but ordinary amidocamphor. Like other diazo-compounds, it gives off all its nitrogen when heated with water or alcohol. On heating it in an oil-bath to  $140^{\circ}$ , it suddenly gives off all its nitrogen, leaving a white crystalline body which smells like common camphor, re-volatilises with steam, and, after complete purification, melts at  $160^{\circ}$ . This body, named by the author dehydrocamphor, has the composition  $C_{10}H_{14}O$ , and its formation may be represented by the equation—



It is isomeric with the two thymols and with carvol. It is no phenol; is insoluble in water, but dissolves in the other ordinary solvents. With phosphorus pentachloride, it reacts only when heated, and without evolution of hydrogen chloride. It has a waxy consistence, melts easily, and distils with vapour of water.

H. W.

**Carbonic Ether of Borneol.** By A. HALLER (*Compt. rend.*, **94**, 86).—When the residue left in the preparation of cyano-borneol is extracted with boiling alcohol, and the solution allowed to cool, yellowish plates separate out. This substance, when pure, forms white plates or hexagonal tables, insoluble in water and alkalis, slightly soluble in cold alcohol, but soluble in boiling alcohol, ether, chloroform, benzene, glacial acetic acid, &c. It melts at  $215^{\circ}$ , and sublimes without decomposition. Its rotatory power varies with that of the borneol from which it is prepared. When fused with potash, or boiled for a long time with alcoholic potash, it yields potassium carbonate and borneol. It is not attacked by nitric acid in the cold, but at  $100^{\circ}$  the two combine, forming an oily liquid. At a higher temperature oxides of nitrogen are given off, and camphor is found. The substance has the composition  $C_{21}H_{34}O_3$ , and is a carbonic ether of borneol,  $CO_3(C_{10}H_{17})_2$ .

C. H. B.

**Compounds of Bismuth Iodide with Organic Bases.** By K. KRAUT (*Annalen*, **210**, 310—327).—These compounds are obtained as precipitates by adding potassium bismuth iodide to a solution of the base in hydriodic acid; the majority are crystalline, varying in colour from orange to dark red; they are decomposed by water, and in many cases by absolute alcohol; some, however, may be crystallised from alcohol in unaltered form. Further, the composition of these precipitates is dependent upon their mode of preparation. The general formula for the most frequently occurring compounds is  $3R'_4NI, 2BiI_3$ , the methylamines, tetramethylammonium, the ethyl derivatives of glycine, piperidine, and dimethylaniline forming compounds of this composition. The methylamines also form compounds, having the general formula  $5R'_4NI, 3BiI_3$ , but with dimethylamine a compound  $2R'_4NI, BiI_3$  was also obtained. Compounds of the form  $R_4NI, BiI_3$  were obtained with triethylamine, acetopiperidine, and dimethylamine;

aniline, meta- and para-toluidine yielded compounds of this form only. Triethylsulphine iodide yields a compound  $2\text{Et}_3\text{SI}, 3\text{BiI}_3$ , also compounds having the formulæ  $3\text{Et}_3\text{SI}, 2\text{BiI}_3$  and  $\text{Et}_3\text{SI}, \text{BiI}_3$ .

Jørgensen (*Jahresb.*, 1869, 717) has already shown that the tetrethyl bases of nitrogen, phosphorus, arsenic, and antimony yield compounds with bismuth iodide, which have the general formula  $3\text{R}_4\text{NI}, 2\text{BiI}_3$ .

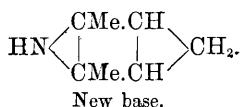
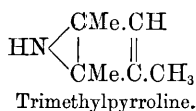
P. P. B.

**A Third Homologue of Pyrroline in Dippel's Oil.** By G. L. CIAMICIAN and M. DENNSTEDT (*Ber.*, 14, 1338—1342).—The non-basic portion of Dippel's animal oil has been shown by the experiments of Weidel and Ciamician to contain homopyrroline and dimethylpyrroline (*Abstr.*, 1880, 403); and from the portion of the crude oil, which boils between  $170^\circ$  and  $200^\circ$ , the authors of the present paper have succeeded in isolating a third homologue of pyrroline, having the composition of trimethylpyrroline. This portion of the oil was first repeatedly boiled with caustic potash to remove nitrils of fatty acids, and then subjected to fractional distillation, great care being taken to separate all that passed over below  $180^\circ$ ; and the higher-boiling oils were collected in two portions, boiling respectively at  $180$ — $195^\circ$  and  $195$ — $205^\circ$ , which were then treated separately. To isolate the new pyrrolines supposed to be present in them, each portion was heated for several days in a reflux apparatus placed in an oil-bath, and lumps of potassium were thrown in from time to time. As the metal disappeared, a dark-brown heavy oil separated at the bottom of the flask, and solidified on cooling to a nearly black, shining, brittle, vitreous mass. The action being ended, the unattacked oil was poured off, and the solid residue, consisting of the potassium-compound of the new pyrroline, was pulverised, washed repeatedly with absolute ether, and decomposed with water to separate the pyrroline homologue. In this way there was obtained a layer of dark-brown oil floating on the water, which, on distillation, passed over with the water, and after careful drying, was fractionally distilled with caustic potash.

The two portions of the crude oil above-mentioned ( $180$ — $195^\circ$  and  $195$ — $205^\circ$ ) were subjected to this series of processes, each by itself, and the pyrrolines obtained from them were fractionally distilled, whereby three fractions were obtained, boiling respectively at  $180$ — $182^\circ$ ,  $188$ — $190^\circ$ , and  $190$ — $195^\circ$ . These fractions all gave by analysis numbers agreeing very nearly with the formula of *trimethylpyrroline*,  $\text{C}_7\text{H}_{11}\text{N} = \text{C}_4\text{H}_2(\text{CH}_3)_3\text{N}$ , which requires 77.06 per cent. C., 10.10 H, and 12.84 N, and the authors regard it as very probable that the portion of the oil boiling at  $180$ — $195^\circ$  contains two isomeric trimethylpyrrolines.

These pyrrolines, when recently distilled, are colourless oily liquids, but on exposure to light and more especially to air, they rapidly turn yellow, and ultimately become black-brown. On paper they leave spots, which, in a few minutes, turn red-brown. They have a rather strong unpleasant odour, somewhat like that of pyrroline itself. They are slightly soluble in water, but dissolve more readily in concentrated mineral acids, and are precipitated therefrom by water and by alkalis. When suspended in water, they give with mercuric chloride a white precipitate soluble in hydrochloric acid. Their hydrochloric

acid solution reduces platinic chloride, and, on boiling, forms a black precipitate. Their vapours redden a deal shaving moistened with hydrochloric acid. They act very slowly on metallic potassium, yielding a brown vitreous compound. Heated with strong hydrochloric acid in a sealed tube for two hours at  $120^{\circ}$ , they appear to undergo a molecular transformation, the base separated from the resulting liquid by potash having the same composition as the original trimethylpyrroline, but exhibiting different properties. The authors represent the transformation by the following formulæ:—



The constitution assigned to this new base is that of a “dehydrolutidine.” The authors promise a further communication on this portion of their results. H. W.

**Quinoline Derivatives.** By L. BEREND (*Ber.*, **14**, 1349—1350).—When 1 mol. quinoline is digested with an equivalent quantity of ethylene bromide in a sealed tube at  $75$ – $80^{\circ}$  for several days, a crystalline mass is obtained; and on dissolving this mass in water, digesting the solution till it no longer smells of unaltered quinoline, evaporating to the crystallising point, subjecting the resulting crystalline mass to strong pressure, purifying it with animal charcoal, and recrystallising from absolute alcohol, concentric groups of thick yellowish needles are obtained, having the composition of *bromethylquinoline bromide*,  $\text{C}_8\text{H}_7\text{NBr} \cdot \text{C}_2\text{H}_4\text{Br}$ , and analogous to the trimethylbromethylum bromide,  $\text{Me}_3(\text{C}_2\text{H}_4\text{Br})\text{NBr}$ , and triethylbromethylum bromide,  $\text{Et}_3(\text{C}_2\text{H}_4\text{Br})\text{NBr}$ , which Hofmann obtained some years ago by the action of ethylene bromide on trimethylamine and triethylamine respectively (*Proc. Roy. Soc.*, **9**, 293). Numerous compounds of analogous constitution have also been obtained by Ladenburg. By agitation with silver chloride, bromethylquinoline bromide is converted into the corresponding *chloride*, which crystallises from hot concentrated hydrochloric acid in orange-yellow needles, and yields a well-crystallised *platinochloride*,  $\text{C}_{22}\text{H}_{22}\text{N}_2\text{Br}_2\text{Cl}_2 \cdot \text{PtCl}_4$ . H. W.

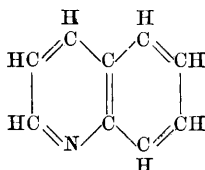
**Morphine.** By E. v. GERICHTEN and H. SCHRÖTTER (*Annalen*, **210**, 396—400).—Morphine, when distilled over heated zinc-dust, yields pyrroline, ammonia, trimethylamine, pyridine, and quinoline, forming together the chief products. Phenanthrene is also formed amounting to about 4 per cent. of the morphine, and a small quantity of a base, which is probably phenanthrene-quinoline. P. P. B.

**Tetrahydrocinchoninic Acid.** By H. WEIDEL (*Monatsh. Chem.*, **3**, 61—83).—This acid, which the author obtained about a year ago as a *hydrochloride*,  $\text{C}_{10}\text{H}_{11}\text{NO}_2 \cdot \text{HCl} + \frac{3}{2}\text{H}_2\text{O}$ , by the action of tin and hydrochloric acid on cinchoninic acid (*Abstr.*, 1881, 830), is converted, on heating the hydrochloride for a considerable time at  $100^{\circ}$  in a sealed tube with acetic chloride, into *acetotetrahydrocinchoninic acid*,  $\text{C}_{10}\text{H}_{10}\text{AcNO}_2$ ; and on opening the tube, distilling off the excess of

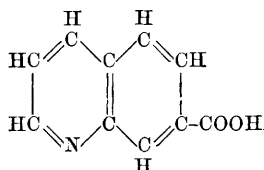
acetic chloride, and expelling the last traces of the latter by heating over a water-bath, the acetyl-derivative remains in the form of a honey-yellow syrup, which, on addition of a little alcohol, solidifies after a while to a crystalline mass, the mother-liquor, when drained off, yielding a further crop of crystals. This product may be purified by crystallisation from dilute alcohol, and finally by several crystallisations from hot water, with addition of animal charcoal. A moderately concentrated solution evaporated over sulphuric acid in a vacuum yields the acetyl-derivative in large, highly lustrous, nearly colourless orthorhombic crystals, exhibiting the combination  $P. \infty P \infty . \infty P \infty$ ; and cleavable parallel to the two pinacoids. Axial ratio  $a : b : c = 0.8477 : 1 : 0.5696$ . Angle  $P' : P$  (vertical) =  $50^{\circ} 26'$ ; (lateral) =  $60^{\circ} 34'$ .

Acetyltetrahydrocinchoninic acid dissolves but sparingly in cold water and alcohol, with moderate facility in the same liquids when warm; it is nearly insoluble in ether. The aqueous solution is not altered by ferric chloride; neither is it precipitated by silver nitrate or by lead acetate. It has a bitter and faintly acid taste. When heated in a capillary tube, it softens at  $157^{\circ}$ , and melts at  $164.5^{\circ}$  to a light yellow liquid, which remains fluid for a long time after cooling, and then solidifies to a crystalline mass. At a higher temperature, the acid turns brown and decomposes, so that it cannot be volatilised without decomposition. It does not contain any water of crystallisation. It does not unite with other acids or with platinic chloride, but it contains a hydrogen-atom replaceable by metals. All its salts that have been examined are soluble in water. The *ammonium* and *potassium* salts crystallise in slender colourless needles, and are very hygroscopic. The *calcium salt*,  $(C_{10}H_9\text{AcNO}_2)_2\text{Ca} + 2\text{H}_2\text{O}$ , obtained by neutralisation, forms a white shining powder, appearing under the microscope as an aggregate of four-sided pointed prisms, which give off their water a little above  $100^{\circ}$ .

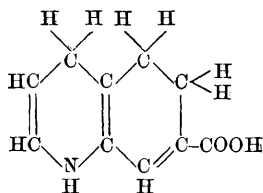
The formation of this acetyl-derivative shows that tetrahydrocinchoninic acid contains the group  $\text{NH}$ , and consequently that in its formation from cinchoninic acid, the hydrogen added enters, partly at least, into the pyridine nucleus of the quinoline molecule.



Quinoline.



Cinchoninic acid.



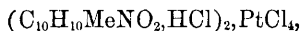
Tetrahydrocinchoninic acid.

*Methyltetrahydrocinchoninic acid*,  $C_{11}H_{13}NO_2 = C_{10}H_{10}MeNO_2$ , is produced by heating the hydrochloride of tetrahydrocinchoninic acid with about three times its weight of methyl iodide at  $100^\circ$  for three or four hours in a sealed tube, whereby two layers of liquid are obtained, the lighter, which is brownish, holding in solution the product of the reaction, while the heavier colourless layer consists of excess of methyl iodide, and methyl oxide resulting from a secondary reaction. On dissolving the contents of the tube in methyl alcohol and leaving the liquid to evaporate, shining yellowish needles and laminæ are obtained, consisting of the hydrochloride or hydriodide of methyltetrahydrocinchoninic acid, from which, after purification by crystallisation from water and agitation with ether, to remove resinous matters, the methylated acid itself may be obtained by agitating the cold moderately dilute solution with levigated silver oxide, till the precipitate, which is at first white, is coloured brownish by excess of silver oxide. The acid, which at ordinary temperatures can dissolve but a very small quantity of silver oxide, is found in the filtrate in the free state, and may be purified from a trace of silver by treatment with hydrogen sulphide and subsequent concentration. On concentrating the liquid further, the acid crystallises in wavelitic groups of slender colourless needles, which may be completely purified by removal of the mother-liquor and one crystallisation from alcohol.

Methyltetrahydrocinchoninic acid thus prepared forms large colourless crystals, of prismatic habit. It deliquesces in water, dissolves very easily in alcohol, but is nearly insoluble in benzene, ether, chloroform, &c. It has a bitterish taste, like that of saltpetre; reddens litmus-paper but very slightly. Its aqueous solution is not altered by ferric chloride, or precipitated by silver nitrate; but on subsequent addition of dilute ammonia, a white precipitate is obtained. It gives a white precipitate with basic lead acetate, none with the normal salt. The crystals turn slightly reddish on exposure to the air. In the air-dried state, they have the composition  $C_{10}H_{10}MeNO_2 + 2H_2O$ , give off half their water in the exsiccator, decompose partly at  $100^\circ$ , and melt with further decomposition at  $169-170^\circ$ .

Methyltetrahydrocinchoninic acid is an extremely weak acid, scarcely able to decompose carbonates; its metallic salts are highly deliquescent. With mineral acids on the other hand, it forms very beautiful compounds, which crystallise with great facility. The *hydrochloride*,  $C_{10}H_{10}MeNO_2 \cdot HCl$ , prepared by evaporating with hydrochloric acid the solution obtained, as above described, by treating the first crude crystallisation with silver oxide, separates from the concentrated solution on cooling, in large shining faintly yellowish crystals, but may be obtained by slow recrystallisation from very dilute hydrochloric acid, in very large perfectly colourless crystals, mostly forming staurolitic intersection-twins, having an almost adamantine lustre. They are monoclinic;  $a : b : c = 1.2955 : 1 : 1.1925$ .  $\beta = 93^\circ 25' 30''$ . Faces,  $\infty P\infty$ ,  $0P$ ,  $P\infty$ ,  $+P\infty$ ,  $\infty P$ , and an undeterminable negative hemipyramid. Cleavage not very distinct. The hydrochloride dissolves readily in water, especially when warm, but less readily than tetrahydrocinchoninic acid itself. At  $100^\circ$ , it turns reddish from incipient

decomposition. The air-dried crystals contain 1 mol. water, which they do not give off in a vacuum. The *platinochloride*,



forms large yellowish-red crystals.

The *hydriodide*,  $\text{C}_{10}\text{H}_{10}\text{MeNO}_2, \text{HI}$ , prepared like the hydrochloride, separates in large crystals having a brownish-yellow colour, due to separated iodine, but may be obtained, by redissolution in water and slow evaporation, in nearly colourless, strongly lustrous, monoclinic crystals, isomorphous with those of the hydrochloride. They contain 1 mol. water, which they give off under the air-pump; the dehydrated compound is very hygroscopic, and decomposes when heated.

By prolonged action of methyl iodide on the hydrochloride of tetrahydrocinchoninic acid, there are formed, in addition to the hydrochloride and hydriodide just described, a number of oily products probably related to the bodies which Hofmann obtained by the energetic acid of methyl iodide on quinoline.

*Oxidation of Tetrahydrocinchoninic Acid.*—This acid, when treated with various oxidising agents—chromic acid, permanganate, silver oxide, nitric acid, &c.—and under the most various circumstances, is not converted, as might be expected, into cinchoninic acid, or into pyridinetetracarboxylic acid, but yields merely a small quantity of a faintly acid syrup, in which after some weeks a few crystals begin to form.

*Action of Nitrous Acid.*—By treating a hot dilute solution of the hydrochloride of tetrahydrocinchoninic acid with a quantity of silver nitrite sufficient to remove the whole of the chlorine, and filtering, a solution is obtained, which on cooling deposits nitrosotetrahydrocinchoninic acid,  $\text{C}_{10}\text{H}_{10}(\text{NO})\text{NO}_2$ , in small, delicate, yellowish-white, shining prismatic needles, melting at  $137^\circ$ , nearly insoluble in cold, soluble in hot water, easily in alcohol, somewhat less readily in ether. By the action of dilute sulphuric acid, this nitroso-compound is resinised, but when treated with strong sulphuric acid, it yields a mixture of sulphonic acids, which are likewise formed directly by the action of strong sulphuric acid on tetrahydrocinchoninic acid itself. These acids have not yet been thoroughly examined, but one of them is a disulphonic acid,  $\text{C}_{10}\text{H}_8(\text{SO}_3\text{H})_2\text{NO}_2$ , and another appears to be a trisulphonic acid.

*Distillation over Zinc-dust.*—Cincholepidine.—A mixture of the hydrochloride of tetrahydrocinchoninic acid with about 30 times its weight of zinc-dust heated to bright redness in a stream of hydrogen yields, together with steam and uncondensable vapours, a distillate of a heavy, light-yellow, basic oil, having an odour of quinoline. This oil is best purified by partial oxidation, for which purpose a solution of the crude distillate in sulphuric acid is diluted with a large quantity of water, and chromic acid is added by small portions as long as volatile products smelling like pyrroline are evolved on heating. The liquid mixed with caustic potash is then distilled in a stream of hydrogen, whereby a milky aqueous distillate is obtained which, after a while, deposits heavy, nearly colourless oil-drops—the separation of which is facilitated by addition of solid potash—and the

oil, after drying with recently fused potash, is repeatedly distilled. After two repetitions of this treatment, the base passes over quite colourless. It smells like quinoline, and dissolves completely and without change of colour in hydrochloric acid, the solution yielding a yellow crystalline precipitate with platinic chloride. The base has a burning taste, is nearly insoluble in water, dissolves readily in alcohol and ether, and boils under ordinary pressure at  $258.6^{\circ}$  (corr.). It has the composition of lepidine,  $C_{10}H_9N$ , and may therefore be called cincholepidine. Its formation appears to take place according to the equation:  $C_{10}H_{11}NO_2 + H_2 = 2H_2O + C_{10}H_9N$ , the yield amounting to about 58 per cent. of the theoretical. Vapour-density [ $H. = 1$ ], 70.9; calc. 71.5. The *platinochloride*,  $(C_{10}H_9N, HCl)_2, PtCl_4$ , is soluble in hot water and in boiling hydrochloric acid, and separates from the latter by slow evaporation in rather large prismatic needles belonging to the triclinic system. The *aurochloride*,  $C_{10}H_9N, HCl, AuCl_3$ , separates on adding auric chloride to a solution of the base in hydrochloric acid, in microscopic slender needles soluble in a large quantity of water and in hot hydrochloric acid, this latter solution depositing it on cooling in light yellow shining prismatic needles, apparently monoclinic.

By oxidation with chromic acid, cincholepidine is converted into cinchoninic acid, according to the equation:  $C_{10}H_9N + O_3 = H_2O + C_{10}H_7NO_2$ . The product, however, amounts to only 20 per cent. of the theoretical quantity, a portion of the cincholepidine being completely burnt.

H. W.

**Attempted Synthesis of Tropine and its Derivatives.** By A. LADENBURG (*Ber.*, **14**, 1342—1349).—In this paper the author describes some experiments which were made with this object, but like those already described (*Ber.*, **14**, 227; *Abstr.*, 1881, 263) did not lead to the desired result.

1. *Valerylene-trimethylammonium Bromide*,  $C_8H_{17}NBr_2$ .—This compound, described in the former paper, is formed from trimethylamine and valerylene bromide. Its solution yields with hydriodic acid a sparingly soluble bromiodide,  $C_8H_{17}NBrI$ , which, however, is more readily prepared by agitating the aqueous solution of the product obtained from valerylene bromide and trimethylamine with recently precipitated silver oxide, and neutralising the filtrate with hydriodic acid. It contains the bromine in a more intimate state of combination than Hofmann's  $Me_3NC_2H_4Br_2$ , from which silver oxide removes all the bromine. By agitating the aqueous solution of the bromiodide with silver chloride, the *bromochloride*,  $C_8H_{17}NBrCl$ , is obtained, from which may be prepared the *aurochloride*,  $C_8H_{17}NBrCl, AuCl_3$ , sparingly soluble and crystallising in shining laminæ, and the *platinochloride*,  $(C_8H_{17}NBrCl)_2, PtCl_4$ , moderately soluble and crystallising in prisms.

2. *Ethylpiperidinemethylene Iodide*,  $C_8H_{17}NI_2$ , prepared by heating ethylpiperidine (b. p.  $126-128^{\circ}$ ) in a sealed tube at  $80-100^{\circ}$  with a molecular proportion of methylene iodide, crystallises from hot water in yellow laminæ, totally unlike hydrotropine iodide, with which it is identical in percentage composition. It is sparingly soluble in cold, very easily in hot water; melts easily under boiling water; melts



with decomposition when heated in the dry state. When agitated in aqueous solution with silver chloride, it exchanges half its iodine for chlorine, forming a chloriodide, from which may be prepared an aurochloride,  $C_8H_{17}NI\cdot AuCl_3$ , separating from hot water in light yellow crystals, and a platinochloride,  $(C_8H_{17}NI\cdot PtCl_4)_2$ , which separates from a concentrated solution in orange-yellow crystals. Silver oxide also removes from the di-iodide only half its iodine.

3. *Dimethylpiperidine Iodide*,  $C_7H_{15}NI_2$ , is formed by direct addition of iodine (6·7 parts) to dimethylpiperidine (3 parts), both dissolved in chloroform, and separates as a nearly colourless precipitate, crystallising from hot water in white prisms. By agitation with silver chloride, it is converted into a chloriodide, yielding with auric chloride the double salt,  $C_7H_{15}NI\cdot AuCl_3$ . When, on the other hand, the iodide is agitated and gently heated with silver oxide, the whole of the iodine is removed, and a base is obtained, called by the author dimethylpiperidine, and having the composition  $C_7H_{13}N$ . On distilling the solution separated from the iodide and oxide of silver, this base passes over between  $137^\circ$  and  $140^\circ$  in the form of an oil. Its solution in hydrochloric acid yields with auric chloride a yellow precipitate, which crystallises from hot water in long needles, having the composition  $C_7H_{13}N\cdot HCl\cdot AuCl_3$ , and with platinic chloride the salt  $(C_7H_{13}N\cdot HCl)_2PtCl_4$ , which crystallises in light red prisms. This base appears to occupy a position intermediate between the piperidine and pyridine series.

4. *Dimethylpiperidine-methylene Iodide*,  $C_8H_{17}NI_2$ , is obtained by direct combination of dimethylpiperidine with methylene iodide at ordinary temperatures, or more readily at about  $55^\circ$  in a sealed tube. It forms compact prisms having the aspect of hydrotropine iodide, and like that compound, melting under water; dissolves readily in hot water, and crystallises out for the most part on cooling. With silver chloride, it reacts like hydrotropine iodide, but differs therefrom essentially in its behaviour to silver oxide, which withdraws from it only half its iodine. The solution obtained by agitation with silver chloride gives, with auric chloride, the salt  $C_8H_{17}NI\cdot AuCl_3$ , which separates as an oil, soon solidifying to small light yellow crystals; and with platinic chloride, the salt  $(C_8H_{17}NI\cdot PtCl_4)_2$ , which crystallises from hot water in long shining orange-red needles.

5. *Propyl- and Isopropyl-piperidine*,  $C_8H_{17}N$ .—These two bases are easily obtained by the action of the corresponding propyl iodides on piperidine. They both boil between  $149^\circ$  and  $150^\circ$ , and have a strong narcotic odour, that of isopropylpyridine being very much like that of tropidine. The author is engaged in converting these bases by oxidation into compounds having the formulæ  $C_8H_{15}NO$  and  $C_8H_{13}N$ , and comparing these products with tropine and tropidine.

H. W.

**Crystalline Hyoscyamine.** By DUQUESNEL (*J. Pharm.* [5], 5, 131—138).—Owing to the discrepancies in the results obtained by various chemists in examining hyoscyamine prepared from the seeds of the henbane, the author has undertaken the following research:—After extracting the freshly-bruised seeds with boiling alcohol ( $90^\circ$ ), acidulated with tartaric acid (1—1000), and distilling the alcohol, the

residue separated into two layers, of which the lower was partly soluble in water, a resinous substance remaining undissolved. The upper layer, equal to one-third of the weight of the seed, consisted of a green oil, from which a considerable quantity of the alkaloid was obtained by shaking with sulphuric acid, nearly neutralising the acid solution with potassium carbonate, filtering, and evaporating the solution over a water-bath to a syrupy constituency. Alcohol is then added, the potassium sulphate separated, the alcoholic solution freed from alcohol by distillation, the residue diluted with water to a syrup, mixed with excess of potassium carbonate and shaken with chloroform. The alkaloid was extracted from the chloroform solution by treatment with sulphuric acid; and the acid solution, decolorised by animal charcoal, was evaporated to a small bulk, and allowed to stand in contact with calcium carbonate. The mixture, after addition of sand, was evaporated over sulphuric acid, and the residue shaken with chloroform. The chloroform solution was reduced to a small bulk, mixed with toluene (to retard the evaporation), and allowed to evaporate, when hyoscyamine was obtained in tufts of long, colourless, prismatic crystals without smell. It is very soluble in chloroform, easily in alcohol and ether, and appreciably in water, to which it imparts a strongly alkaline reaction. It resembles atropine in its reactions, emitting an odour of bitter almonds or hawthorn when treated with potassium dichromate and sulphuric acid, and giving a violet coloration after treatment with nitric acid, evaporating the excess of acid and adding alcoholic potash. Its physiological action is more rapid and of longer duration than that of atropine. The further study of its chemical and physical properties is reserved.

L. T. O'S.

**Action of Soluble Ferments.** By A. WURTZ (*Compt. rend.*, **93**, 1104—1106).—Finely divided fibrin digested for some time with a dilute solution of pepsin, then washed with water and digested at 38° for two days with hydrochloric acid of 0.4 per cent., dissolves almost completely, leaving only a slight residue. The liquid, when mixed with an equal volume of alcohol and filtered, yields a solution of peptone, not precipitated by nitric acid. Fibrin digested for the same time, with acid of the same strength, also dissolves, but the solution, after adding alcohol, gives an abundant precipitate with nitric acid, the fibrin having been converted into syntonin and not into peptone. Casein, precipitated from fresh milk by dilute hydrochloric acid after removal of the fat by means of ether, when digested with papaine or pepsin, washed and treated with water, yields a mixture of insoluble dipeptone and casein-peptone, very soluble in water and not precipitated by nitric acid. It is evident that papaine and pepsin can combine, in an insoluble form, with certain albuminoid substances, so modifying the latter that they undergo hydration in pure water at 40° with formation of true peptones.

C. H. B.

**Peptone.** By A. POEHL (*Ber.*, **14**, 1355).—The author finds that all proteids are converted into peptone by contact with animal and vegetable tissues, as first observed by Eichwald (1873) in the case of liquid albumin. The conversion of swollen fibrin into peptone by the

action of the tissue of the lungs or kidneys takes place as energetically as under the influence of pepsin. Eichwald's view that between the genuine proteids and the peptones there exist gradual states of transition depending only on different states of hydration, is corroborated by the fact that peptone is reconverted into precipitable albumin by treatment with dehydrating agents, such as alcohol and alkali-salts.

H. W.

**On Gluten.** By T. WEYL and BISCHOFF (*Bied. Centr.*, 1881, 826).—It was attempted to determine whether gluten existed ready-formed in flour, or whether its formation was due to the action of water on a "gluten-forming" substance. No formation of gluten having been observed in the residue after the myosin had been removed by means of a 15 per cent. sodium chloride solution, it is concluded that myosin is the gluten-forming compound. Flour heated at 60° for several hours appears to lose the faculty of forming gluten; it is therefore concluded that the absence of gluten was not due to the want of a ferment, but to the coagulation of the albuminoid matter. E. W. P.

**Phrenosin.** By J. L. W. THUDICHUM (*J. pr. Chem.* [2], 25, 19—28).—Phrenosin is prepared from the white matter which separates on cooling an alcoholic extract of the brain, by submitting it to repeated fractional crystallisation from alcohol, and precipitation of phosphorised bodies by lead acetate and by cadmium chloride; the phrenosin, kersasin, and cerebrous acid remaining in solution are then separated by repeated fractional crystallisation from much alcohol, which on cooling to 28° deposits chiefly phrenosin. Phrenosin,  $C_{41}H_{79}NO_8$ , is white, tasteless, and odourless, it crystallises from absolute alcohol in white rosettes; when treated with sulphuric acid at the ordinary temperature it first turns yellow, then forms a purple liquid from which flocks separate. By long-continued heating of phrenosin with dilute sulphuric acid, the following substances were obtained:—

*Cerebrose*,  $C_6H_{12}O_6$ , a sugar, forms hard white crystals: it reduces Fehling's solution, 6 parts of cerebrose having the same reducing power as 5 parts of glucose. Its specific rotatory power in aqueous solution = + 70° 40'. On heating cerebrose with dilute sulphuric acid, it yields *cerebrosic acid*,  $C_6H_{10}(H_2)O_6$ , which does not reduce alkaline copper solutions.

*Sphingosine*,  $C_{17}H_{35}NO_3$ , is a crystalline alkaloïd; it is insoluble in water, soluble in alcohol or ether. The sulphate has the formula  $2(C_{17}H_{35}NO_2).H_2SO_4$ ; the hydrochloride,  $C_{17}H_{35}NO_2.HCl$ , crystallises in spear-shaped needles.

*Neurostearic acid*,  $C_{18}H_{36}O_2$ , isomeric with stearic acid, forms fine white needles (m. p. 84°), and is soluble in ether. *Ethyl neurostearate*,  $C_{18}H_{36}O_2Et$ , prepared by boiling phrenosin with alcohol and sulphuric acid, is crystalline, soluble in alcohol and ether, and can be distilled in a vacuum.

By heating phrenosin for only a short time with hydrolysing reagents an alkaloïd, *psychosine*,  $C_{23}H_{45}NO_7$ , is obtained. It is crystalline, soluble in water and alcohol, gives a purple coloration when heated with sulphuric acid, and is completely precipitated from its solutions by excess of hydrochloric or nitric acid.

*Esthesine*,  $C_{35}H_{69}NO_3$ , a feebly basic substance, crystallises in hexagonal tables, and is soluble in ether; it may be regarded as phrenosin from which the elements of cerebrose have been split off.

When phrenosin in aqueous or alcoholic solution is heated with sulphuric acid for a short time only, it unites with water forming a *hydrate*, apparently  $C_{41}H_{81}NO_9$ .

From these results, phrenosin may be regarded as formed by the union of 1 mol. each of sphingosine, neurostearic acid, and cerebrose, with elimination of 2 mols. of water. A. J. G.

**Remarks on the Paper "On some New Brain Derivatives."**  
**By Eugen Parcus.** By J. L. W. THUDICHUM (*J. pr. Chem.* [2], 25, 29—41).

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## Physiological Chemistry.

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**Filtration of Albuminous Solutions through Animal Membranes.** By E. GOTTWALT (*Zeits. Phys. Chem.*, **4**, 423—436).—The experiments were made in two ways:—(1.) The column of liquid was at rest. (2.) The liquid to be filtered was allowed to flow over the membrane under different pressures. In both cases, the amount of the filtrate and the quantity of serum, albumin or globulin, it contained was calculated per hour and per c.c. Ureters from fresh human bodies were used as membranes.

The amount of the filtrate was found to increase with the pressure, but in no definite ratio. The permeability of the membrane diminished during the experiment, and did not improve by the use of a lower pressure. The amount of albumin in the filtrate was always less than in the original fluid, *e.g.*, egg albumin solution gave 72 per cent.; fluid from an ovarian cyst 70 per cent.; blood serum, 60 per cent.; hydrocele fluid, 40 per cent. The percentage of globulin was still less, serum albumin and serum globulin passing through the membrane in the ratio of 3 to 2. By the second method, similar results were obtained, only more marked. The following table shows the figures obtained by filtering blood serum containing 6.024 per cent. albuminoid.

Pressure. centim.	Time.	Amount of filtrate. grams.	Proteids. per cent.	Filtrate per hour. per c.c.
80	hour	6.885	5.075	0.161
60	"	5.453	4.083	0.127
40	"	4.520	3.019	0.106
30	"	3.111	3.015	0.073
20	"	2.114	2.001	0.049

The apparatus used is figured in Hoppe-Seyler's *Lehrbuch der Physiol. Chem.*, Part. I, p. 156.

W. N.

**The Carbonic Acid of Muscle.** By R. STIRITZING (*Pflüger's Archiv.*, **23**, 151—161).—The experiments recorded in this paper are a repetition of a previous series made by the author. The same apparatus was used, and great care was taken to make the various parts as perfect as possible. The mean values obtained for the  $\text{CO}_2$  in vol. per cent. of muscle were as follows:—

Muscle quickly cooled .....	7.2	per cent.
„ tetanised and quickly cooled ..	6.6	„
„ tetanised and slowly cooled ....	13.5	„
„ washed.....	2.7	„
„ kept at 50° C. in the warm chamber and then washed .....	2.0	„
„ neither warmed nor washed ....	15.4	„

W. N.

**Formation of Acid, and the Amount of Lactic Acid in Muscle.** By ASTASCHEWSKI (*Zeits. Phys. Chem.*, **4**, 398—406).—Comparisons were made between tetanised and untetanised muscles of rabbits with regard to the amount of lactic acid contained in them. In order to avoid *post-mortem* changes, the muscles were placed in absolute alcohol and mixed in it. Free lactic acid could only be found in traces in muscle at rest. Lactic acid in combination was found in greater quantity in resting than in tetanised muscle, as zinc lactate, 0.275 per cent. and 0.244 per cent., as against 0.186 per cent. and 0.066 per cent.; from paralysed muscles, 0.488 per cent. The alcoholic extract of resting muscle was somewhat greater than that of tetanised muscle. The acid of muscle does not dissolve in alcohol, but in water, and is, as Liebig conjectured, acid potassic phosphate. The acidity of the watery extract of the muscles after treatment with alcohol was estimated. That of paralysed and resting muscle was found to be higher than that of tetanised muscle; the figures obtained were 0.234 per cent., 0.173 per cent., 0.221 per cent., 0.243 per cent., as against 0.140 per cent., 0.126 per cent., 0.143 per cent., and 0.198 per cent. The watery extract of tetanised muscle was found to be less than that of resting muscle; in this the author's results agree with those of Helmholtz and Ranke.

W. N.

**Influence of Tetanus on the Acids contained in Muscle.** By J. W. WARREN (*Pflüger's Archiv.*, **24**, 391—406).—The author compared the quantities of lactic acid and lactates in tetanised and untetanised muscle, by mincing them finely, extracting with alcohol, evaporating the extract, and again extracting with ether after acidifying with sulphuric acid. The lactic acid remaining after evaporation of the ether was estimated by titration with soda. Great care was taken to avoid *post-mortem* changes. The animal was immediately after death packed in ice and salt. As soon as the whole body was frozen hard, the muscle to be investigated was removed, minced fine, and allowed to stand 24 hours in absolute alcohol, and the process of extraction was then repeated.

100 grams of muscle taken from three rabbits killed by bleeding, yielded 0.119 gram lactic acid; 100 grams from three tetanised rabbits

yielded 0.077 gram; in a second experiment, the figures were 0.208 gram and 0.070 gram respectively. Similar results were obtained by comparing the limbs of the same animal, one being tetanised and the other not.

Taking the acidity of the untetanised limb at 1, that of the tetanised limb was found to be 0.548—0.639—0.520. Experiments on frogs yielded the same or similar results, *i.e.*, the acidity of the tetanised limb was found to be only half that of the untetanised one.

In a note appended to the paper, Pflüger explains the apparent paradox on the theory that two molecules of lactic acid condense into one, with elimination of water, the acidity as measured by the power of saturating alkali being at the same time reduced to one-half.

W. N.

**Action of the Liver on Peptone.** By J. SEEGEN (*Pflüger's Archiv.*, **25**, 165—176).—The investigations of the author and Kratschmer tend to show that the sugar in the liver increases after death to an extent not to be accounted for by the transformation of the glycogen present. In the liver extracts they very frequently found a body insoluble in alcohol, and laevorotatory. Seegen took liver pulp, and treated two equal portions with distilled water and peptone solution respectively, at 17° C., and estimated the sugar in each after the lapse of one hour, and again 96 hours after, and in all cases he found the sugar in the portion mixed with peptone solution greater than that in the other preparation; the increase in the quantity of sugar amounted to 0.5 per cent. of the weight of the liver on the average; longer digestion seemed to diminish the amount of increase. Extracts of kidneys, lung, and spleen appeared not to have this effect.

W. N.

**Formation of Sugar in the Liver.** By J. SEEGEN and F. KRATSCHEMER (*Pflüger's Archiv.*, **24**, 467—484).—The object of this paper is by further experiments to meet the many objections offered to the statement put forward by the authors, that the liver sugar has some other source than glycogen. Two dogs' livers were used and investigated at intervals of 72 and 96 hours.

(1.) Glycogen :	beginning of experiment ..	10.1	per cent.
	end ..	10.2	"
Sugar :	beginning ..	0.4	"
	end ..	3.3	"
(2.) Glycogen :	beginning ..	8.86	"
	end ..	8.44	"
Sugar :	beginning ..	0.51	"
	end ..	2.30	"

From these figures they argue that the sugar must have some other source than glycogen. An experiment on a young fox is in their opinion conclusive. The result was as follows:—

Glycogen two minutes after death, 0.7 per cent.; sugar, 0.79 per cent.; an hour later, sugar, 1.83 per cent.; 24 hours later, sugar, 1.98 per cent. More sugar was therefore formed than the glycogen in the liver could possibly account for.

W. N.

**Post-mortem Formation of Sugar in the Liver.** By R. BOEHM and A. F. HOFFMANN (*Pflüger's Archiv.*, **23**, 205—219).—The authors raise a series of objections to the conclusion arrived at by Seegen and Novak, that the liver-sugar has some other source than glycogen, and they especially object that the conclusion was drawn, not from direct estimation of glycogen and sugar, but from indirect processes, which render it possible that something other than sugar was reckoned as such. They insist that the sugar of the liver has no other origin than glycogen, and refer to a previous experiment in which they obtained the following results:—One-half of the liver of a cat yielded 1·65 gram sugar, and 16·91 grams glycogen = 20·52 grams sugar; the other half examined three hours later contained 3·2 grams sugar and 15·95 grams glycogen = 20·9 grams sugar; the difference between these results falls within the limits of error. The results of two new experiments are then given:—

Liver of	1st Piece.			2nd Piece 24 hours later.		
	Glycogen.	Sugar.	Total as sugar.	Glycogen.	Sugar.	Total as sugar.
Cat .....	6·883	1·976	9·623	5·511	3·440	9·563
Dog .....	5·346	1·950	7·889	2·595 and 1·085 dextrin	3·796	7·883

The difference in the two sets of totals is so insignificant that the authors believe it to be impossible that the sugar could have had any source other than the glycogen. W. N.

**Composition of Ewes' and Goats' Milk.** By A. VOELCKER (*Bied. Centr.*, 1881, 858).

	Ewe.			Goat.		
	Rich.	Poor.	Colostrum.			
Water .....	75·00	86·12	69·74	82·02	84·48	83·51
Fat .....	12·78	2·16	2·75	7·02	6·11	7·34
Casein .....	6·58	5·59	17·37	4·67	3·94	3·19
Lactose .....	4·66	4·93	8·85	5·28	4·68	5·19
Ash .....	0·98	1·20	1·29	1·01	0·79	0·77
Nitrogen in casein....	100·00 1·05	100·00 0·89	100·00 2·78	100·00 0·78	100·00 0·63	100·00 0·57
Specific gravity .....	—	—	1·036	1·0357	1·0302	1·0302

E. W. P.

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**Physiology and Pathology of the Elimination of Urea.** By H. OPPENHEIM (*Pflüger's Archiv.*, **23**, 446—504).—(1.) *Urea Elimination under various Conditions.—Normal Condition.*—The experiments were made on the author. He found that on a diet consisting of 400 grams bread, 300 grams meat, and 950 grams milk, the urea elimination in four days became very constant, the variations averaging 1 gram. The mean of seven days' observation gave 34.6 grams = 16.2 grams N; 1.1 gram was passed in the faeces; the total was: N of food = 18.9 grams, N excreted 17.3 grams: difference 1.6 gram retained in the body.

(2.) *Distribution of the Urea Elimination over the Day.*—The maximum corresponds to the time of taking the largest amount of albuminoids as food.

In one period of 24 hours, 34.80 grams were eliminated, i.e., 1.45 gram per hour. In the first four hours after the midday meal 0.24 gram was eliminated per hour in excess of the average; in the following four hours during which a meal not containing much nitrogen was taken, 0.54 gram above the average was excreted. During the night the hourly excretion fell below average.

(3.) *First Stage of Inanition.*—During a fast of 24 hours 23.91 grams were eliminated, i.e., 10—11 grams below average. The body weight also fell 1 kilo.

(4.) *Influence of Large Quantities of Fluid.*—4 litres of water taken in 24 hours increased the urine by 3000 c.c., the urea by 5 grams. Nearly the whole effect was produced by 2 litres taken at the mid-day meal.

(5.) *Influence of Coffee.*—This, apparently, produces a slight diminution on two days; without coffee, 33.21 grams and 33.60 grams were eliminated respectively; on the day on which coffee was taken, 31.97 grams were eliminated.

(6.) *Influence of Quinine.*—2 grams of quinine raised the daily elimination in one case nearly 4 grams, and in a second 4.5 grams.

(7.) *Influence of Excessive Perspiration.*—Excessive perspiration induced by the subcutaneous injection of 0.02 gram pilocarpine, produced no effect on the urea elimination.

(8.) *Influence of Muscular Work.*—The author quotes authorities on the generally received opinion, that muscular work does not produce any increase in the elimination of nitrogen unless the supply of carbohydrate material for the purpose fails. He thinks the investigations of Frankel on the effect of dyspnoea, which tend to show that with diminished oxygen there is an increased proteid metabolism, are borne out by his own experiments. The ascent of the Kreuzberg, near Bonn, gave as the mean of six experiments 34.91 grams per diem; pulse, 90; respiration, 16 per minute. A single ascent, so conducted as to give rise to dyspnoea (pulse 140—150), gave 36.64 grams as a result, and a second 39.71. A prolonged walk on the level, without any increase of frequency in the respiration, gave 34.44 grams, the next day (rest) 33.81 grams, the day after (forced labour) 39.01 grams, the next day (rest) 35.89 grams.

*Urea Elimination in Pathological Conditions.*—In a case of phthisis the author found the urea excreted to be in excess of the nitrogen of the

food ; on some days more than double in a case of acute parenchymatous nephritis ; the urea was also high in proportion to the food.

W. N.

**Phosphoric Acid in the Urine of Ruminants.** By C. LEEUW (*Bied. Centr.*, 1881, 855).—In the urine of oxen fed on brewers' grains, 0.93—1.13 per cent. phosphoric acid was found ; lime was also present.

E. W. P.

**Albuminoids of the Vesicula Seminalis in Guinea-pigs.** By H. A. LANDWEHR (*Pflüger's Archiv.*, 23, 538—541).—The author finds that the secretion of the *glandula seminalis* of guinea-pigs contains a body having the properties of fibrinogen.

W. N.

**Researches on Splenic Fever.** By FESER (*Bied. Centr.*, 1881, 856).—The poison of splenic fever in the form of spores of the anthrax parasite withstand dryness and cold. Animals prone to this fever can withstand successfully the introduction only of small quantities of the infected matter. Inoculation renders animals capable of resisting the infection of the stem- or spore-shaped parasites. Phenol camphor, boric and salicylic acid, borax, alum, and ferrous sulphate are useless as curative agents or disinfectants. The amount of infecting matter introduced determines the period and course of the fever.

E. W. P.

**Fate of Morphine in the Animal Body.** By E. LANDSBERG (*Pflüger's Archiv.*, 23, 413—433).—The author used the method of Uslar and Erdmann for the detection of morphine ; but, despite the observation of all the precautions indicated by Kaugmann, he failed to detect morphine in the urine of a dog poisoned with it. On the recommendation of Wislicenus, 0.2 gram of pure morphine and 0.3 c.c. of acetic acid was added to 50 c.c. of urine and the whole evaporated to a syrup on the water-bath. The cooled mass was then extracted with alcohol. The alcohol had a yellow colour, and left a resinous residue on evaporation which was now extracted with absolute alcohol. The alcoholic extract was again evaporated, the residue treated with distilled water containing a few drops of dilute acetic acid ; the acid solution was then shaken with amyl alcohol at 70°, fresh portions being used, and the operation repeated until a perfectly clear and colourless solution was obtained. The amyl alcohol was then removed by a separating funnel, the acid solution again evaporated, treated with hot amyl alcohol, and made alkaline. The amyl alcohol extracts were then evaporated on the water-bath, and the brown residue, weighing 0.2766 gram, was submitted to various reactions. A small portion of the residue placed on a slide under the microscope, treated with dilute hydrochloric acid, and left to evaporate, yielded crystals whose form and reaction with Fröhde's reagent left no doubt as to the presence of morphine. The remainder was dissolved in water saturated with ammonia, and allowed to stand for 24 hours, a brown crystalline precipitate formed which, when dried, weighed 0.094 gram, representing about 50 per cent. of the morphine originally added to the urine.

Experiments were then made with dogs which were poisoned with morphine, either in the form of hydrochloride or sulphate.

(1.) 0.20 gram morphine hydrochloride was injected subcutaneously, and 26 hours after, although the effects of the poison had been most marked, the author failed to detect morphine in 100 c.c. of urine.

(2.) 0.40 gram were injected on one day, and 0.20 gram on each of the two following days. Morphine could not be detected in the urine.

(3.) A large dog took 2.50 grams morphine hydrochloride, but it could not be detected in the urine.

(4.) After injecting 0.80 gram morphine hydrochloride into the jugular vein, 90 c.c. of the urine of the next day gave the morphine reactions, although the author failed to find it in the blood three hours after the injection.

From these experiments, the author concludes that only a part of the morphine taken into the stomach is absorbed, while part gets involved in the fæces and is so lost. When, however, the poison is injected subcutaneously, he is of opinion that the alkaline blood destroys and decomposes it, so that only very minute traces of morphine or, at the most, the products of its decomposition, can be detected in the urine.

W. N.

**Phosphorus Poisoning in Hens.** By A. FRÄNKEL and F. RÖHMANN (*Zeits. Physiol. Chem.*, **4**, 439—450).—The experiments were made during fasting, and the phosphorus administered in the solid form in a bread pill. The excreta were collected and weighed, and the water, nitrogen, and uric acid in them estimated. The three experiments made show a very apparent increase of tissue change.

*Experiment I.*—1st and 2nd day (simple fasting) 1.1 gram nitrogen was eliminated; on the 4th and 5th day 0.58 gram; on the 6th and 7th day (after phosphorus had been given) the nitrogen rose to 1.29 and 1.71 gram. The uric acid showed a similar increase. The results in the 2nd and 3rd experiments were even more marked; of the nitrogen in experiment II, before the phosphorus was given, 28.07 per cent. was due to uric acid. After phosphorus was given 71.7 per cent.; an enormous diminution in the number of red blood-corpuscles was also observed to follow the administration of the phosphorus.

W. N.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Origin and Function of certain Microzymas.** By A. BÉCHAMP (*Compt. rend.*, **92**, 1344—1347).—The author terms *microzymas* certain molecular granulations which appear in various fermentations before any other organised production, which exist in a great number of rocks, calcareous and otherwise, and in all the centres of activity of living organisms whether animal or vegetable. He has endeavoured to trace their origin, and to find out, if possible, the part they play in the natural world.

1. *Microzymas and Bacteria from Marsh Lands*.—Whenever vegetable and animal detritus accumulates beneath the surface of water, there bacteria and isolated microzymas are to be found. They were very abundant in the basin containing aquatic plants in the Jardin des Plantes at Montpellier, and on careful examination were found to give off nitrogen, carbonic anhydride, and marsh-gas. By distillation of 50 litres of this water, sufficient alcohol and acetic acid could be obtained to permit of easy recognition.

2. *Microzymas from Building Land and Pot-mould*.—Earth from the environs of Montpellier was levigated with creasoted water, and the imperfectly separated microzymas were made to act as ferments upon sugar and starch. The fermentation of sugar was very slow, lasting for nearly two years; alcohol and acetic acid were produced without any trace of butyric acid, but the residue from the distillation was acid, and doubtless contained tartaric acid. With starch, alcohol and butyric acid were found in abundance together with acetic and lactic acids.

The mould used in the Jardin des Plantes is crowded with microzymas mixed with bacteria. 15 grams of this fine earth were introduced into 500 grams of thin starch-paste and set aside for three months; at the expiration of this time it was examined, and there were separated alcohol; sodium acetate, 5 grams; crude butyric acid, 8 grams; calcium lactate, 10 grams.

In a somewhat similar manner *road-dust*, which contains no traces of bacteria, was shown to be loaded with microzymas; it readily induced fermentation, and alcohol and acetic acid were obtained from the decomposition of the organisms without the intervention of sugar or starch.

In all phenomena of slow combustion or *eremacausis*, it is easy to prove the presence of molecular granulations, similar to, if not identical with, microzymas. Thus, a dead cat was buried in a quantity of pure chalk, and the whole enclosed in a glass vessel. It was kept for six years and then opened; there remained of the cat nothing but a few fragments of the vertebral column and some of the larger bones. The portions of the chalk which were taken from the top inner layers dissolved, without residue, in dilute hydrochloric acid, but the lower layers upon which the animal originally lay were full of microzymas. The chalk from the latter rapidly liquefied starch-paste, converting it into alcohol, acetic and butyric acids, and when treated with hydrochloric acid, was not wholly soluble, the microzymas being left behind. The principal difference which the author has made out between the microzymas obtained from the dead animal, and those originally existing in the chalk, is that, under similar conditions, the former are easily converted into bacteria, whilst those from the chalk never change their form.

The conclusions drawn from the foregoing investigations are, that the microzymas which are to be found in chalk, in rocks, in earth, in road-dust, or in marshes, have their origin in the microzymas, which form an integral part of every living organism; their physiological function, after death, is the total destruction of this organism, and, this necessary destruction being effected, they remain, according

to circumstances, imbedded in the soil or distributed through the air, where perhaps they fulfil other at present unknown functions.

In connection with this subject, the following is a reply to a note of M. Béchamp, by Chamberland and Roux (*ibid.*, 1347), in which they deny the existence of the *microzyma cretæ*. They state that as the result of experiments which were instituted with a view of ascertaining if natural chalk could give rise in appropriate media, to various fermentative actions, and especially to the lactic and butyric fermentations, they have never been able to induce any fermentation whatever, or to obtain any microscopic organisms. They consider that Béchamp has not taken all the precautions necessary to eliminate causes of error which are inherent to this class of investigations; nothing is easier than to obtain the results described by Béchamp; it is simply necessary to take no further precautions than he has taken, for all the causes of error resulting from organic germs foreign to the chalk, germs in the air, in the water, and on the surface of the vessels used, are favourable to the success of fermentative experiments, such as he has brought forward. They are of opinion that, if Béchamp reproduces his former experiments under more careful and exact conditions, he will find that his new results will be in accordance with their own; that is to say, he will obtain neither fermentation nor production of microscopic organisms. They conclude by saying that geologic microzymas have no existence.

Pasteur, however, inclines to the existence of microzymas. In the *Bull. de l'Acad. de Méd.*, 20, 627, he says: "In our experiments, we have noticed this remarkable circumstance—that all natural earths which we have had occasion to examine contain germs capable of inducing a peculiar fermentative or septic action." J. W.

**Chemical Distinctions between Living and Dead Proto-plasm.** By O. LOEW and T. BOKORNY (*Pflüger's Archiv.*, 25, 150—164).—Different varieties of freshwater algæ have, as the authors have determined, the power of precipitating metallic silver from alkaline solutions. This power exists only during life, and disappears at death. The silver solution used in these experiments contained 1 part silver nitrate in 100,000 parts of water. For its preparation 13 c.c. of caustic potash solution of sp. gr. 1.33 and 10 c.c. ammonia solution of 0.964 sp. gr. were mixed and diluted to 100 c.c.

1 c.c. of this solution and 1 c.c. of a 1 per cent. silver solution were mixed and diluted to a litre; the solution was found to react even when made 10 or 20 times weaker. Aldehyde and benzaldehyde reacted with this solution, pyrogallol and quinol with a solution of 1 part silver nitrate in 12,000 of water, formic acid with 1 in 1000. No known body was found to react with a solution of 1 in 1,000,000. Spirogyra and Zygnema were the algæ experimented on, and these were grown in spring water containing 0.1 per cent. of dipotassic phosphate and ammoniac nitrate. The zygnema plants, when gently dried between filter-paper, yielded—

Albuminoïds .....	2·806 per cent.
Fat with lecithin and chlorophyll.	0·010 „
Glucose .....	0·111 „
Starch, &c.....	6·077 „
Ash .....	0·009 „
Water .....	90·387 „

A very short time after being placed in the silver solution, the algæ became dark-coloured from deposited silver; in 12 hours some cells were quite black, and very few showed no deposit. Exposure for five minutes to a temperature of 50° C. sufficed to destroy this property, as also an hour's immersion in a 1 per cent. solution of copper sulphate, of sulphuric acid, or of soda, or by exposure to ether vapour. Immersion in a watery solution of quinine acetate, 0·2 per cent., had no effect, nor had solution of veratrin. This property of protoplasm was observed also in *Chladophora*, various plant-hairs, and in the roots and growing stalks of phanerogams. Negative results were obtained with growing yeast and *mucor*. The authors are of opinion that the results are dependent on the presence in living protoplasm of some members of the aldehyde-group. W. N.

**Aldehyde Nature of Living Protoplasma.** By O. LOEW and T. BOKORNY (*Ber.*, 14, 2508—2512).—This communication is part in answer to Reinke (this vol., 243). The authors have distilled portions of the algæ, *zygnema* and *spirogyra*, with water, collected the first few c.c. of distillates, tested them, and found no reduction of silver, and therefore infer that if formaldehyde is the first product assimilated by living plants that it (at least in these cases) is so quickly used up, that not even a trace of it is to be found. The reducing action of the distillate from poplar and willow is, they think, possibly due to the presence of salicylaldehyde (or a derivative thereof), which they point out is volatile with steam in spite of its high boiling point,—Reinke having suggested that the reducing body could not be an aromatic aldehyde because of the high boiling point of the latter.

The authors then state that this reducing power is not due to sugar or tannin, which are frequently present in plants, several cells having no sugar at all possessing this power, and moreover living cells reduce alkaline silver solution, which are by far too dilute (containing  $\frac{1}{3000000}$  Ag) to be affected either by sugar or tannin. And further, they maintain that the reducing substance is not soluble in water, for the cells lose this property when they are killed by means which remove no perceptible quantity of soluble substances, besides the living cells produce greater reduction in weak ( $\frac{1}{157000}$ ) than in concentrated ( $\frac{1}{1570}$  Ag) alkaline silver solutions, which can be accounted for from the fact that the cells are killed quicker in the latter case. Moreover, the microscopic examination shows that the cell-juice, which filters out, on account of the contraction of plasma-tubes caused by the reaction, never contains metallic silver. As this power of reduction, as a rule, ceases when the plant is killed, the authors consider that it is only the living protoplasm, or the active

principle of the albumin of the cell, which contains the aldehyde group, and that it really is only a function of this protoplasm. When, however, the plant is killed by an alkaloid (strychnine) the silver reducing power is retained in a marked manner; this anomaly is thus explained: the strychnine (its presence is easily recognised in the cells) combines with the active albumin, and hence prevents the removal of the aldehyde group; but if this combination is destroyed, as, for example, by the action of dilute acids or alkalis or of tannin, then also the aldehyde group can and does disappear. D. A. L.

**Relation between the Decomposition and Formation of Carbonic Anhydride.** By J. B. LAWES (*Bied. Centr.*, 1881, 851).—The amount of carbon as carbonic anhydride which per acre and year is given to the air of Great Britain is reckoned at 3942 lbs. from burnt coal, 300 lbs. from imported material, and 1275 lbs. from home produce, making in all 5517 lbs. The weight of carbon as carbonic anhydride resting over every acre of land is 14,000 lbs., therefore in three years, by reason of fresh additions, the quantity would more than double itself but for some compensating influence. As the plants cannot consume all the excess of carbonic anhydride, it is thought that the ocean absorbs a very large proportion, which, even at considerable depths, is known to contain this gas. E. W. P.

**Occurrence of Salicylic Acid in the Violaceæ.** By K. MANDELIN (*Pharm. J. Trans.*, 12, 627—628).—Salicylic acid in the free state occurs in the leaves, stems, and rhizomes of the different varieties of *V. tricolor* and in *V. sylvatica*, whilst the petals and seeds contain only traces of the free acid, and a substance which on boiling with hydrochloric acid yields salicylic acid. The leaves of the *V. odorata* do not contain any of the acid, but on boiling the rhizomes with hydrochloric acid, salicylic acid is readily detected, and is present probably as a glucoside. In the other varieties of the *Violaceæ*, salicylic acid is present only in traces, or entirely absent.

The property of salicylic acid to prevent germination probably accounts for the fact that only traces of the free acids are found in the seeds.

The quantity of acid in the different varieties varies from 0.1441 to 0.0829 per cent. calculated on the dried herb free from ash.

Besides salicylic acid, the presence of a body giving an intense yellow colour with alkalis and a precipitate with basic lead acetate was detected. L. T. O'S.

**Analysis of a Wheat Plant-ash.** By A. CAVAZZI (*Bied. Centr.*, 1881, 857).—In the ash of a wheat plant there was found—

K <sub>2</sub> O.	MgO.	CaO.	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> . (Mn <sub>2</sub> O <sub>4</sub> ).
26.98	12.34	3.01	56.39	0.62	0.62	0.04 pts. p. c.

E. W. P.

**Perishing of Wheat, Rape, and Clover in Winter.** By C. BREYMAN (*Bied. Centr.*, 1881, 829—833).—An agricultural paper in



which the causes of the perishing of young wheat, &c., during the winter are detailed, and methods are proposed which shall reduce the loss thus occasioned.

E. W. P.

**Action of Frost on Evergreens.** By J. W. MOLL (*Bied. Centr.*, 1881, 858).—When leaves are frosted, the ice exists either on the surface or in the intercellular space; this causes an alteration in the colour to a dark green. The ice is formed from the water in the cells, out of which it is forced, but returns when the ice thaws; then the original colour is assumed. When the leaf is thawed, a partial vacuum is formed in the intercellular space. The leaves when frozen hang downwards, but when thawed recover their normal position in about 7—30 minutes.

E. W. P.

**Valuation of Fodders.** By A. LECLERC and others (*Bied. Centr.*, 1881, 816—823).—Leclerc reduces the starch-equivalent of fat in fodders from  $2\frac{1}{2}$  to 2, and considers that the relative prices of carbohydrates, fat, and albuminoids should be 1 : 2 : 6. The value of the non-nitrogenous constituents is reckoned at 0.08 M. per kilo., and that of the albuminoids at 0.48 M. A calculation is given to show how, by the use of these figures, a close approximation to market prices is obtained. J. König finds that the value of the food-constituents varies each year with the value of fodder, so that each season necessitates a fresh valuation: A. Mayer considers that the value of the three constituents in fodders remains the same, and that the value of the fodder must be determined by what it contains; but this is unsatisfactory, for the same constituents in different foods have not the same feeding value; digestibility, palatability &c., exercising a considerable influence.

On comparison of linseed cakes of approximately like value, and containing equal amounts of albuminoids and carbohydrates, but different percentages of oil, it appears that the value of 1 kilo. oil must be reckoned at 0.22 M., and that 1 kilo. of oil in palm-nut cake costs 0.16 M. In the same way, it is shown that 1 kilo. carbohydrates in turnips and potatoes costs 0.11 M.; and by substitution of the value of fat and carbohydrates for their percentages in rape and palm-cake the value of albuminoids is obtained; this value is 0.3 M. per kilo.

E. W. P.

**Cultivation of Soja Bean.** By STAHEL and others (*Bied. Centr.*, 1881, 837—842).—A series of papers in which the cultivation of the soja bean is advocated as a prolific and remunerative crop, not only useful for cattle, but also, when boiled or roasted, as food for man.

E. W. P.

**Chevalier Barley.** By J. S. WAGNER (*Bied. Centr.*, 1881, 828).—Chevalier barley is shown to be the best sort, when grown under favourable conditions.

E. W. P.

**Linseed Cakes and Linseed Meal.** By HOLDEFLEISS (*Bied. Centr.*, 1881, 823).—This paper calls attention to the adulteration of linseed cakes and linseed meal with various other meals, as that of rape cake, &c.; also a table is given showing the very great variation which may

exist between various samples as regards the percentage of oil (5—17·5 per cent.).

Although the German cakes are less rich in oil than those imported, they are frequently to be preferred, because the imported cakes have generally a higher percentage of water, and although richer in oil, the oil is liable to be rancid.

E. W. P.

**Cultivation of Potatoes, and the Feeding Value of Various Sorts.** By C. SCHMEHL and others (*Bied. Centr.*, 1881, 833—837).—By comparing the yields of various kinds of potatoes, Schmehl finds that Yellow Rose on a heavy soil does well, but that Richter's Imperator is backward, and Gleason's seed is very liable to disease. Giraud, out of 32 sorts, finds Magnum Bonum and Early Rose the best. Nessler, out of 96 kinds, finds that the Saxon "Zwiebel" potato has the highest percentage of starch (20·5), then Late Rose and Biscuit.

E. W. P.

**The High Percentage of Phosphoric Acid in Volcanic Soils.** By RICCIARDI (*Bied. Centr.*, 1881, 852).—The author does not agree with Gasparin, that the fertility of volcanic soils is due to the large amount of phosphoric acid which they contain. There is far more acid present than is necessary, as  $\frac{5}{100000}$  is quite sufficient for growth; but the fertility is rather due to favourable climate and high percentage of organic matter, which sometimes amounts to 20 per cent.

E. W. P.

**Coarse and Fine-grained Superphosphates.** By F. FARSKY (*Bied. Centr.*, 1881, 853).—The activity of superphosphates is dependent on the fineness of the grain; the finer the grain the smaller is the yield of the crop, the coarser grains always containing more soluble phosphate than the fine, although they may be part of the same sample; moreover, the soluble phosphate in the fine-grained sample is the most readily absorbed by clay soils.

E. W. P.

**Deportment of Various Phosphates in the Soil.** By HOFFMEISTER (*Bied. Centr.*, 1881, 813—816).—The plots, 15 in number, were  $\frac{1}{30}$  morgen in size, and the manures applied in triplicate, 1 kilo. of phosphoric acid being applied in each case. The results showed that reduced phosphates were as good in their action as the soluble phosphates in the soil, which was a sterile sandy soil, very poor in lime. To determine the depth to which applied phosphates sank in the soil, boxes containing the same soil as that of the experimental plots were sunk, and exposed freely to the weather; after a top dressing of various phosphates, it was found that the phosphates had not descended more than 10 cm., although in the case of a "super," phosphoric acid was found at a depth of 20 cm. Also it was noticed that dicalcium phosphate remained unaltered during the experiment, and that in such a soil the monocalcium phosphate was not converted into the tribasic compound.

E. W. P.

**Analysis of Mud.** By J. KÖNIG (*Bied. Centr.*, 1881, 853).—Mud from the town-moat of Munster contained 59·27 of air-dried substance,

and in this dry matter there were present: 0·6 per cent. N, 0·704  $P_2O_5$ ; 0·419  $K_2O$  (soluble in HCl); 0·512  $K_2O$  (soluble in  $H_2SO_4$ ); 13·17  $CaCO_3$ ; and 48·37 sand.

E. W. P.

**On Marl, Sea Mud, &c.** By J. KÖNIG (*Bied. Centr.*, 1881, 854).  
—Analyses of marl, sea mud, and residues from Lahn phosphorite factory.

E. W. P.

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## Analytical Chemistry.

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**A New Eudiometer.** By N. SOKOLOFF (*Jour. Russ. Chem. Soc.*, 1882, 56—62).—The instrument is a modification of Doyère's gas-pipette. Two platinum wires are sealed into the top of the graduated receiver, which has the form of an ordinary eudiometer, and is surrounded by water, in order to keep its temperature constant. The measurements and explosions can be made in the same vessel, so that it is unnecessary to transfer the gas into a separate eudiometer, except for absorptions. The arrangement will be easily understood by a reference to the drawing in the original paper. It allows of quick operations, the results of which are very satisfactory. B. B.

**Apparatus for Fractional Distillation.** By W. HEMPEL (*Zeits. Anal. Chem.*, 20, 502).—Instead of the fragile Henninger-Le Bel tube, the author uses a long wide glass tube, filled with solid glass beads. The cooling effect of the latter is such that it is possible, by means of this simple contrivance, to obtain alcohol of 95 per cent. from 18 per cent. alcohol, by a single distillation, provided the operation be conducted slowly. O. H.

**Absorption of Oxygen by Metallic Copper.** By W. HEMPEL (*Zeits. Anal. Chem.*, 20, 499).—Metallic granulated copper moistened with a solution consisting of equal parts of a saturated solution of ammonium carbonate and ammonia solution of 0.93 sp. gr., absorbs rapidly and completely large quantities of oxygen from gaseous mixtures. The author utilises it as an absorbent in gas analysis, and declares his method to be preferable to the pyrogallol process. O. H.

**A New Method for the Quantitative Estimation of Chlorides in the Urine, with a Note on the Chemistry of Mercury.** By L. HABEL and J. FERNHOLZ (*Pflüger's Archiv.*, 23, 85—126).—In a solution of urea containing sodium chloride, a solution of mercuric nitrate gives a permanent precipitate, only so soon as the whole of the sodium chloride is decomposed by the mercurial solution into mercuric chloride and sodium nitrate. Liebig's method for the estimation of chlorides in urine is based on this fact, and the authors chiefly concerned themselves with testing it. The experiments were made with urea, sodium chloride, and mercuric nitrate, prepared and purified with every possible precaution; the results were all too high, the error amounting

in neutral solutions to 18.5—25.3 per cent., and in solutions acidified with nitric acid to as much as 24.5 per cent., and even 37.1 per cent. Naturally estimations of urea corrected for chlorides estimated in this way would also be in error 2—8 per cent.

Far too low a value was obtained by operating on urine treated with baryta mixture if it was neutralised, a little too high if it was made acid. For the determination of the true amount of chlorides present, the method of titration with silver after fusion with soda and potassic nitrate was adopted, direct estimation of chloride with silver in the urine after treatment with baryta, did not give concordant results; the average error was 8 per cent. too high. On the other hand, the authors found that direct titration could be carried out if the urine was acidulated with nitric acid. A special method was used. 15 c.c. of the urine and baryta mixture were taken, neutralised with nitric acid, then 10 drops of nitric acid (sp. gr. 1.119) were added, and afterwards the silver solution (1 c.c. = 0.01 gram sodium chloride), so long as any precipitate fell. A small portion was then filtered into a test-tube, and a drop of silver solution added; if a decided opalescence was obtained, the test portion was returned to the original liquid, and 0.1 c.c. of the silver solution added, and the test again applied until the opalescence obtained was no longer marked; an equal quantity was then filtered into another test-tube, and two drops of a 1 per cent. solution of sodium chloride added; if the opalescence obtained in this case was equal to that in the former, the right point was reached. The experiment was repeated by mixing in the whole of the silver solution at once, and applying the test to filtered portions as before; if in this case there was a decided difference between the opalescence produced in the two test portions, then another experiment was made, using less or more silver solution, as was indicated. The results are stated to agree very closely together, and the authors claim that the method is more rapid than Neuhaven's method of fusion, the amount of silver necessary to precipitate the chlorides being thus determined. A second portion of 15 c.c. of the urine and baryta mixture was taken, and the chlorides precipitated; the urea was then estimated by Liebig's method, no correction for chlorides being required. The results were very satisfactory.

W. N.

**Further Investigations on the Quantitative Determinations of Chlorides in Urine treated with Baryta Mixture and Acidified with Nitric Acid.** By L. HABEL (*Pflüger's Archiv.*, 24, 2).—

The author finds the method described by himself and Fernholz difficult of application to dog's urine, as the silver precipitate blackens very quickly owing to the formation of sulphide; this may be in a great measure avoided by very quick filtration. The results tend to be too high. There is no trouble with the urine of horses, oxen, and guinea-pigs. For the urine of animals generally, a silver solution of such a strength that 1 c.c. = 0.005 gram NaCl was found to be most convenient.

W. N.

**Decomposition of Silicates by Bismuthic Oxide.** By W. HEMPEL (*Zeits. Anal. Chem.*, 20, 496).—Lead oxide has been proposed by S. Bong (*Bull. Soc. Chim.*, 29, 50) for the decomposition of sili-

cates, in order to render them soluble in acids. On account of the difficulty experienced in obtaining absolutely pure lead oxide, the author proposes to substitute for it bismuth nitrate, as this occurs in commerce in a state of purity, and offers the advantage of remaining solid at the temperature at which it loses its nitric acid. 0.5 gram of silicate is mixed with 10 grams of the nitrate, the mixture gently heated until red vapours cease to escape, the temperature being then raised until the mass is fused, in which condition it is kept for about ten minutes. The product is heated with strong hydrochloric acid, the silica then separated as usual, and from the solution the greater part of the bismuth removed by precipitation with water, the rest with sulphuretted hydrogen. The analysis is then proceeded with as usual.

O. H.

**Detection of Sulphur.** By R. BRUNNER (*Zeits. Anal. Chem.*, 20, 390).—If a little strong potassium hydroxide solution and a few drops of commercial nitrobenzene and alcohol are added to a substance containing sulphur, a red coloration will after some time appear, in consequence of the reduction of the nitrobenzene.

O. H.

**Estimation of Phosphoric Acid in the Ashes of Plants.** By E. v. RAUMER (*Zeits. Anal. Chem.*, 20, 375).—Attention is drawn to the fact that during incineration, a not inconsiderable quantity of pyrophosphate is formed, and a corresponding deficiency in the amount of  $P_2O_5$  found is occasioned, unless care is taken to again convert the pyro- into the ortho-phosphate before precipitating with magnesia or molybdic solution.

O. H.

**Estimation of Potash in Potassium Sulphate.** By WEST (*Zeits. Anal. Chem.*, 20, 387).—For the accurate determination of potash in the sulphate, it is necessary to convert the latter into the chloride by means of barium chloride. The precipitated barium sulphate invariably carries down with it some of the potash, and a correction has to be made to obtain correct results.

At Stassfurt, the determination is carried out as follows:—10 grams of the salt are dissolved in 350 c.c. of boiling water, and 25 c.c. of 25 per cent. HCl. By very careful addition of barium chloride to the boiling potash solution, the whole of the sulphuric acid is removed, and in a fraction of the potassium chloride solution thus obtained, the amount of potash is determined as described in a former paper (*Zeits. Anal. Chem.*, 20, 190). It is found by experience that each cubic centimetre of  $BaSO_4$  thrown down (10 grams of  $K_2SO_4$  yielding 2.99 c.c. of  $BaSO_4$ ) carries down with it twice as much potassium as is contained in 1 c.c. of the solution made up to 500 c.c. Hence a correction is made by calculating from the amount of sulphuric acid contained in the salt, the volume of the barium sulphate, and making up the total volume of the solution to 500, less that volume of  $BaSO_4$ .

O. H.

**Analysis of Metallic Zinc.** By O. GÜNTHER (*Zeits. Anal. Chem.*, 20, 503).—100 grams of the sample to be analysed are treated with successively added small quantities of hydrochloric acid, so that a

little of the zinc remains undissolved. The residue contains all the lead, copper, cadmium, and some iron and zinc. It is treated with pure nitric acid, the solution evaporated, the residue taken up with water, and the insoluble matters (sand, slag, coke, and some antimonious oxide) separated by filtration. From the filtrate, the lead is precipitated by sulphuric acid, and the copper and cadmium by sulphuretted hydrogen, and separated by any of the ordinary methods. In the filtrate from the sulphuretted hydrogen precipitate, the iron is oxidised by bromine, and precipitated as oxide, together with a little zinc, by careful addition of ammonia, the iron oxide being obtained in a state fit for weighing by redissolving and again precipitating.

The chlorine is determined in a second quantity of 100 grams of the material dissolved in pure nitric acid, the sulphur, antimony, and arsenic in another quantity of 100 grams by carefully dissolving it in dilute sulphuric acid, pure zinc being added towards the end of the operation. The gas evolved is first passed through a solution of cadmium cyanide in potassium cyanide, the precipitated cadmium sulphide being weighed; then through silver nitrate solution, in which  $\text{SbH}_3$  causes a precipitation of  $\text{SbAg}_3$ , while  $\text{AsH}_3$  separates metallic silver. The precipitate is collected, heated with dilute nitric acid, the  $\text{Sb}_2\text{O}_4$  weighed, and the silver determined in the solution. From the amount of the latter the percentage of arsenic may be calculated after subtraction of an amount proportional to that of the antimony found.

O. H.

#### Preparation and Use of Ammonium Molybdate Solution.

By KUPFFERSCHLÄGER (*Bull. Soc. Chim.*, [2], **36**, 644—648).—It is a matter of indifference whether the ammonium molybdate solution is poured into the nitric acid, or *vice versa*, provided the liquids are sufficiently dilute, and are mixed gradually, with continual agitation. The deposit which forms in solutions of ammonium molybdate in nitric acid consists of yellow anhydrous molybdic acid, with small quantities of ammonium nitrate. Its formation is due to the presence of nitric acid, and the use of too little water.

The following recipe differs only from that of Champion and Pellet in that the ammonia and nitric acid are more dilute. 10 grams molybdic acid are dissolved in 15 c.c. ammonia diluted with 30 c.c. of water and the solution poured little by little into 50 c.c. nitric acid diluted with 50 c.c. of water. The liquid is allowed to stand for some hours at 40—45°, and then filtered. The solution thus obtained is very sensitive, and will remain clear for two months. If the molybdic acid is free from phosphoric and arsenic acids and from silica, it is preferable to add the ammonium molybdate directly, *without previous acidification*, to the strongly acid solution containing the phosphoric or arsenic acid to be estimated.

The different methods of using the solution, viz. (1), to pour the dilute acid solution of phosphoric or arsenic acid into an excess of ammonium molybdate in nitric acid, agitate briskly, and allow to stand for some time at 40—45°; (2) to add the ammonium molybdate dissolved in nitric acid to the strongly acid solution to be tested; (3) to dissolve the substance in excess of nitric or hydrochloric acid, add excess of ammonium molybdate (not in nitric acid), and *boil*; all

give equally good results, provided the molybdic acid is in excess, and the solution is free from tin, lead, silver, antimony, and organic matter, especially tartaric acid, the addition of which has been recommended by Fresenius.

C. H. B.

**Volumetric Determination of Molybdic Acid.** By F. MAURO and L. DANESI (*Zeits. Anal. Chem.*, **20**, 507).—0.2 to 0.5 gram of the substance are dissolved in a small stoppered bottle in 2.5 c.c. of hydrochloric acid of 1.2 sp. gr. The air is then removed from the bottle by a current of carbonic anhydride, and 1.5 gram of potassium iodide dissolved in an equal weight of water is added. The bottle is then heated for  $1\frac{1}{2}$  hours in a water-bath, the solution diluted with much water, and the liberated iodine titrated by means of hyposulphite. 144 parts of  $\text{MoO}_3$  liberate 127 of iodine.

The numerous test experiments quoted gave very satisfactory results.

O. H.

**Detection of Nickel and Cobalt.** By E. DONATH and J. MAYRHOFER (*Zeits. Anal. Chem.*, **20**, 386).— $\text{NiO}$  remains unaltered when heated with caustic alkalis and iodine, whilst  $\text{CoO}$  is oxidised with the formation of  $\text{Co}_2\text{O}_3$ . Hence, if the precipitated sulphides of nickel and cobalt are dissolved in nitric acid, the solution precipitated with potash, the precipitate heated with iodine, and the oxides then be extracted with ammonia and ammonium chloride, only the nickel will go into solution, and may be recognised in it by triammonium sulphide.

O. H.

**Fresenius-Babo's Test for Arsenic.** By W. FRESENIUS (*Zeits. Anal. Chem.*, **20**, 522).—This method was formerly acknowledged to be capable of indicating smaller quantities of arsenic than any other toxicological methods, and was considered to be of special value on account of the ease with which arsenic and antimony can be distinguished by it. Gradually, however, the opinion of writers on toxicology has become more and more unfavourable, until lately it has been condemned as being incapable of furnishing indications of very minute amounts of arsenic.

The author shows that these adverse criticisms were due to the various so-called improvements and simplifications of the method which had been made by the critics themselves, and he insists that only the original directions, as contained in R. Fresenius' manual of quantitative analysis, lead to good results.

O. H.

**Analysis of Manganese Dioxide.** By A. WAGNER (*Zeits. Anal. Chem.*, **20**, 493).—It is proposed to heat a weighed quantity of the very finely divided ore with a mixture of chromic oxide and sodic carbonate in a combustion tube, to determine the chromate formed, and to calculate from the amount of the latter the value of the dioxide. Only one test experiment is given, with results closely agreeing with those of Fresenius-Will's method.

A similar method is also proposed by the author for the valuation of bleaching powder, but no proof of applicability of the plan is furnished.

O. H.



**Tests for Ferric and Cupric Salts.** By A. WAGNER (*Zeits. Anal. Chem.*, 20, 349).—The following quantities of iron and of copper can be detected when a few drops of the solutions are tested in a watch-glass.

	Fe.	Cu.
With potassium ferrocyanide	$\frac{1}{500}$ mgrm.	$\frac{1}{200}$ mgrm.
Sulphocyanide .....	$\frac{1}{1600}$ "	
Tannin .....	$\frac{1}{300}$ "	
Ammonia .....	—	$\frac{1}{25}$ "
Potassium sulphocarbonate .	—	$\frac{1}{900}$ "

O. H.

**Water Analysis.** By A. WAGNER (*Zeits. Anal. Chem.*, 20, 323).—The author professes to determine the organic substances in drinking water, by separating the "total solids" into parts insoluble and soluble in water, and igniting the former by itself, the latter after the addition of a little cane-sugar. The loss on igniting the insoluble matters, after recarbonisation, is taken as organic matter, whilst the diminution of weight which the soluble substances undergo expresses the weight of soluble organic matters plus the difference in the equivalents between nitric and carbonic acids. This latter may be calculated from the amount of nitric acid actually determined, and after subtraction leaves the loss on ignition due to actual organic matter.

The author draws attention to the deposition of sulphuric acid and ammonium sulphate on platinum vessels, when water is evaporated in them over the naked gas flame, and to the possible errors due to this circumstance.

O. H.

**Tests for Nitrates in Potable Waters.** By A. WAGNER (*Zeits. Anal. Chem.*, 20, 329).—The ferrous sulphate reaction allows of the detection of 0.5 mgrm. of potassium nitrate after previous concentration of the water, but in presence of chloride the reaction is much less delicate. By means of indigo,  $\frac{1}{800}$  mgrm. may be detected without previous concentration. The author condemns all methods which are based on the reduction of the nitrates by means of zinc or other metals, and subsequent testing for nitrites with iodide and starch, as very liable to mislead, and not giving reactions with less than 5 mgrms. of potassium nitrate per litre.  $\frac{1}{500}$  mgrm. may be detected without previous concentration by means of brucine: equally delicate is the diphenylamine test.

He also proposes the reaction with brucine as a means for the quantitative determination of nitrates.

O. H.

**Comparison of the Oxygen with the Organic Matter in Natural Waters.** By T. WEYL and X. ZEITLER (*Zeits. Physiol. Chem.*, 4, 329).—The authors hoped to be able to establish a relation between the oxygen and organic matters in natural waters, but did not succeed; two different samples gave absolutely unsatisfactory results.

W. N.

**Sulphuric Acid in Beer.** By G. F. REISENBICHLER (*Bied. Centr.*, 1881, 863).—Free sulphuric acid in beer may be introduced by sul-

phured hops, and by calcium sulphate, which is frequently employed in breweries.

E. W. P.

**Estimation of Solid Matter in Wines.** By E. MAUMENÉ (*Bull. Soc. Chim.*, [2], 36, 654).—The author agrees with other observers that the residue left by the evaporation of wine at 100° is not of definite value. The inorganic salts retain more or less water, and it is advisable to dry the residue at a higher temperature in order to render them anhydrous. Care must, however, be taken not to decompose the organic matter. For *comparative* estimations, sufficient for commercial purposes, it suffices to dry the residue at 100° until two successive weighings agree without 1—2 centigrams.

C. H. B.

**Testing of Wines.** (*Bied. Centr.*, 1881, 863).—A teaspoonful of the wine is placed in a test-tube and shaken up with 12 drops of basic lead acetate. The resulting precipitate, brought on to white blotting paper, will show the following colours:—

Pure wine, blue-grey.	Carmine, dirty violet-red.	} without zone.
Fuchsine, dirty violet-red with red zone.	Beetroot, ditto.	
Bilberries, indigo-blue.	Cochineal, blue.	
Elderberries, dirty green.	Pernambuco wood, dirty dark-violet.	
Campeachy wood, dirty dark blue.	Litmus, dingy dark blue.	

E. W. P.

**Detection of Glycerol.** By E. DONATH and J. MAYRHOFER (*Zeits. Anal. Chem.*, 20, 379).—The authors, after enumerating and criticising the various methods which have been proposed for the detection of glycerol, recommend the following plan:—The liquid to be tested is evaporated on the water-bath, with addition of caustic lime and sand. The powdered residue is exhausted with a mixture of equal parts of alcohol and ether, the solvent removed by evaporation, and the residue heated very carefully to 120°, with two drops of phenol, and the same quantity of concentrated sulphuric acid. The melt is treated with a little water, and that part which is insoluble in it is rendered slightly ammoniacal. The beautiful red coloration of glycèrein will at once appear if glycerol be present.

O. H.

**Estimation of Glycerol in Beer.** By CLAUSNITZER (*Bied. Centr.*, 1881, 863).—In a tared basin on a water-bath are to be warmed 50 c.c. of beer; the gas having passed away, 3 grams slaked lime is to be added, and the whole evaporated to a syrup; then 10 grams coarse marble is added, and stirred in until all is in lumps and dry; then, after weighing, the contents of the basin are powdered, and an aliquot portion extracted at 88° for four hours with 20 c.c. alcohol; the extract is then mixed with 25 c.c. anhydrous ether, and, after standing, is filtered into a weighed flask, and the precipitate washed with alcohol-ether. The glycerol will be found in the flask after volatilisation of the ether: it should afterwards be ignited, and the ash determined.

E. W. P.

**Precautions required in Using Knapp's Solution for Estimating Sugar; the Reduction of Cupric Oxide by Grape-sugar in Neutral Solutions.** By W. MÜLLER and J. HAGEN (*Pflüger's Archiv.*, **23**, 220—223).—(1.) The authors find it necessary in the titration of sugars by Knapp's method to dilute the mercurial solution, and add the sugar solution in successive portions. If the fluid be not diluted, the results are always too low; rapidity of working is also necessary, as the mercury redissolves.

(2.) If a solution of grape-sugar is boiled for 8 to 15 hours with hydrated cupric oxide, a greenish-blue filtrate of acid reaction is obtained, which, on boiling, yields a precipitate of cuprous oxide. By prolonged boiling, the whole of the copper can be obtained in this form; the oxidation of the sugar also gives rise to the formation of acids.

W. N.

**Quantitative Estimation of Glycogen, Dextrin, and Amylum.** By F. KRATSCHMER (*Pflüger's Archiv.*, **24**, 134—164).—The differences between glycogen in the pulverulent and horny form are discussed by the author in detail; the former contains water, the greater part of which it will give up to sulphuric acid, but reabsorbs it on exposure to air. This water may amount to 13 to 15 per cent. Taking Abele's formula for water-free glycogen, the composition of this pulverulent form would be represented by the formula  $C_{18}H_{30}O_{15} + 4H_2O$ . If glycogen containing water is dried very rapidly at  $115^\circ$ , it is slightly altered, and the solution reduces Fehling's solution. The alcohol in which glycogen precipitated from an acid watery solution has been standing, has a slight reducing power. The precipitation of glycogen from an aqueous solution, by excess of absolute or 95 per cent. alcohol, is as nearly as possible complete; precipitation by glacial acetic acid, on the other hand, is not complete; treatment of glycogen solution with small quantities of hydrochloric acid, did not greatly increase the error, but the addition of any considerable quantity, especially if it were allowed to act for some time, produced a marked effect, the error amounting to as much as 8 per cent. Albuminous precipitates carry down glycogen very readily, and the loss in the preparation by Brücke's method is very considerable. The indirect method of estimating glycogen by conversion into grape-sugar gave very good results when the solution was treated with 1 per cent. hydrochloric or sulphuric acid in sealed tubes kept for 24 hours at  $100^\circ C$ . Six hours was found to be long enough when the acid was 2 per cent. strength. Admixture of albuminoids, *e.g.*, watery extract of spleen or kidney, did not affect the result. The estimation may be made either by titration with Fehling's solution, or by fermentation. The results obtained by the polarisation method were not very consonant.

For the quantitative estimation of glycogen in tissues, if Brücke's method of extraction is used, all excess of acid must be avoided, and the albuminous precipitate must be washed with water on the filter until the filtrate gives no opalescence on the addition of absolute alcohol. The glycogen should then be dried at a gentle heat, increased by degrees to  $115^\circ C$ .

W. N.

**Microscopical Examination of Flour; a Method for the Easy Separation of Tissue Substances.** By C. STEENBUCH (*Ber.*, 14, 2449—2451).—The method consists in getting rid of the starch grains by converting them into dextrin and maltose, by the action of diastase. The diastase is prepared by mixing 20 grams of ground malt with 200 grams of cold water, and, after an hour, with frequent shaking, filtering. 20 grams of the flour are made into a homogeneous magma with 30—40 grams distilled water, and then about 150 grams of boiling water are stirred in; the temperature is allowed to sink to 55—60°, and is kept at that, 30 c.c. of the filtered malt extract being added. In ten minutes, this mixture is poured into a large quantity of water, which is then poured off from the deposit at the bottom; the latter is then digested at 40—50°, or simply shaken with a 1 per cent. soda solution to destroy albuminous matter. The residue consists of the required substances, mixed with a small quantity of unaltered starch granules.  
D. A. L.

**A New Milk-tester.** By H. DANGERS (*Bied. Centr.*, 1881, 842).—A short account of Heeren's pioscope, which consists of a plate of ebonite, in the centre of which is a shallow depression. A few drops of milk are placed in this, and a glass plate is pressed down upon it, clear at the centre, but tinted in the outer portions according to an arbitrary scale, and labelled "cream," "poor," &c. A rough estimate can thus be made of the quality of the milk, when that seen under the clear glass is compared with the tested section adjoining.

E. W. P.

**Adulteration of Butter.** By JOHANSON and others (*Bied. Centr.*, 1881, 848).—Butter frequently contains added water to the amount of 30 per cent. This is to be detected by shaking up 5 grams of butter with 25—30 c.c. petroleum spirit in a burette; after removal of the clear supernatant liquid, fresh petroleum spirit is added; then, after clearing, the amount of water can be read off in the lower part of the burette. Mayer states that considerable quantities of suet, margarin and earth-nut oil, are imported for manufacturing butter; but that butter adulterated with such substances can be detected by taking its density at 100°, at which temperature pure butter has a higher density than the other fats and oils.

E. W. P.

**Detection of Skatole.** By L. BRIEGER (*Zeits. Phys. Chem.*, 4, 414—418).—Separation from indole is of the first importance. The author's process is as follows.—The putrid albuminoïd mixture is distilled with acetic acid, the distillate neutralised and shaken with ether, the ether residue is treated with water, and then with hot picric and hydrochloric acids. The crystalline mass which separates out is then distilled with aqueous ammonia. A mixture of indole and skatole then crystallises out; the separation is effected finally by dissolving these in absolute alcohol, and adding 8 to 10 volumes of water. Indole is more soluble than skatole in alcohol so diluted, and remains in solution, the skatole being precipitated. The author is of opinion that skatole is a constant product of the decomposition of animal proteïds by putrefaction.

W. N.

**Quantitative Estimation of Quinine.** By J. E. DE VRIJ (*Pharm. J. Trans.*, **12**, 601—603).—This is a claim for priority for the estimation of quinine as iodo-sulphate described by A. Christensen (*ibid.*, November, 1881, 441). For the preparation of iodo-sulphate of quinoïdine and the application of the method, see this Journal, 1876 [i], 964. L. T. O'S.

**Incompletely Oxidised Sulphur in the Urine.** By R. LEPINE (*Proceedings of the International Medical Congress*, London, 1881).—The fact that the urine of man and of many animals contains sulphur in a state of incomplete oxidation, has been observed by Voit, Schmiedeberg, Meissner, Sertoli, Salkowski, Munk, Külz, and others. Thudichum and Strumpell have also made the same observation in cases of typhus. For the quantitative determination of this sulphur, many observers have been content to treat the urine with zinc and sulphuric acid, and estimate the sulphuretted hydrogen evolved. Lepine is of opinion that this method is highly unsatisfactory, and that only by some powerful oxidising agents, such as nitric acid and potassium chlorate, can the total amount of sulphur present in the urine be rendered accessible. He cites an experiment in which he found, by the ordinary methods, 3 grams of sulphuric acid in a litre. A second litre, boiled with nitric acid and potassium chlorate, yielded 3·4 grams, and a third yielded, by fusion of the solids with potassium nitrate and sodium carbonate, 3·6 grams, thus showing, that unless active reagents are employed, a large amount of sulphur may be overlooked. This sulphur, oxidised with difficulty, is generally regarded as arising from biliary compounds in the urine, particularly derivatives of taurine. The amount varies under different circumstances, *e.g.*, it is large in constipation. The author quotes authorities (Huppert and Schiff) to the effect that under certain conditions the taurine of the bile is reabsorbed from the intestine, and suggests that the sulphur in the urine which resists oxidation, may be of considerable pathological importance.

In a second paper, the details of experiments on taurine are given. These serve to illustrate the extreme difficulty of oxidising this body completely in solution: less than one-third apparently undergoing decomposition. Bromine in the cold was found to have no action.

Taurocarbamic acid was also tried, and Salkowski's opinion as to the extreme difficulty of oxidising this body fully confirmed.

Taurine was given to a dog (3 grams), and the sulphur estimated in the urine with the following results:—

	Per litre.
Nitrogen evolved by sodium hypobromite.....	8·0 grams
Sulphuric acid pre-existing as such .....	3·35 „
„ obtained by treating with potassic chlorate and nitric acid .....	3·67 „
„ by bromine in the cold .....	4·11 „
„ by fusion with potassic nitrate..	9·68 „

The figures illustrate the author's point, that the quantity of sulphur in the urine oxidisable with difficulty is considerable.

W. N.

**Testing of Liqueurs.** (*Dingl. polyt. J.*, **243**, 165.)—In testing liqueurs—especially *Kirsch- und Zwetsch-wasser*, containing 44—52 per cent. alcohol—Nessler reports that the presence of lime proved qualitatively does not form any criterion as to purity. A large number of liqueurs were analysed as to the presence of free acid; this was found to vary between 9.03 and 0.05 per cent. Pure kirschwasser is coloured blue by the addition of tincture of guaiacum; the coloration is said to be due to copper extracted from the distilling vessels, and to hydrocyanic acid. D. B.

**Detection of Blood-stains.** By DRAGENDORFF (*Pharm. J. Trans.*, **12**, 586—587).—This is a description of methods of manipulation to be adopted in the detection of blood-stains.

The particles of dried blood are first removed, and the scraped spot is used in the following tests:—

(a.) A small piece of moistened filter-paper is pressed on the spot for from 5 to 30 minutes; then moistened with oil of turpentine, which has been exposed to the air, and a drop of a fresh tincture of guaiacum. The blue colour should appear in a few minutes.

(b.) A portion of the spot is treated with a few c.c. of a cold saturated borax solution at 40° C., and examined spectroscopically. Oxy-hæmoglobin, which it is argued may be confounded in this test with red inks from cochineal, a colouring matter from the feathers of the banana-eater, and purpurinsulphonic acid, since they yield similar spectra, may easily be distinguished from the first, which is decolorised by chlorine-water without yielding a precipitate, and from the second as it does not yield the spectrum of reduced hæmoglobin when treated with sodium sulphide (1 in 5); purpurinsulphonic acid yields a spectrum only when the solution is hot.

(c.) The guaiacum test is applied to the solution in borax if the spectroscopic test succeeds.

(d.) A portion of the solution is diluted with 5 to 6 volumes of water and precipitated with zinc acetate solution (5 per cent.). The precipitate is washed, dissolved in 1—2 c.c. glacial acetic acid, and examined spectroscopically for hæmatin.

(e.) A small quantity of the precipitate from (d) dissolved in acetic acid is treated on a slide with a crystal of sodium chloride, allowed to dry by exposure to the atmosphere, and examined for hæmin crystals.

(f.) A portion of the dried blood which has been scraped from the spots is next tested as in (e), and then the guaiacum test applied. The substance may also be tested for nitrogen; but ferric oxide, which absorbs ammonia, as well as wool, silk, &c., may here be sources of error. Blood may be detected on rusty iron by digestion with borax solution at 80°, and spectroscopic examination for hæmatin after warming the solution with acetic acid.

(g.) The source of the blood may be determined, if fresh, by the size and shape of the corpuscles, but in partially decomposed or dried blood the results are unreliable. Thin fragments may, however, be examined by soaking it in turpentine or some other liquid which does not act on the corpuscles. After removing the hæmoglobin, the residue is treated with iodine for the detection of fibrin. Hairs, fish-

scales, &c., often indicate the origin of the blood, and the blood of some animals when warmed with dilute sulphuric acid, often evolves the odour peculiar to the animal, especially so in the case of fish, pig's, and cat's blood. Epithelium cells and sarcinia frequently denote blood from the stomach, whilst that from abscesses contains fat, pus-corpuscles, and cholesterin; in cases of violent defloration or stupration, epithelium cells and spermatozoa should be searched for.

The older the stain is, the more difficult is it to extract the hæmoglobin. A solution of arsenious acid dissolves a spot one or two days old in about a quarter of an hour; eight days' old, in half an hour: two to four weeks, in one to two hours; four to six months, in three to four hours; a year old, in eight hours.

Borax solution may be used to extract blood from soils; and in the case of blood diluted with water it may be precipitated with zinc acetate, when 1 part in 6000 of water or in 1000 of urine may be detected.

L. T. O'S.

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## Technical Chemistry.

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**Technical Chemical Notes.** By G. LUNGE (*Dingl. polyt. J.*, **243**, 157—162).—The experiments described were carried out in the Zurich laboratory by the students.

*Decomposition of Sodium Sulphate by Calcium Bicarbonate.*—According to Pongowski, the sulphates of the alkalis are said to be converted into calcium sulphate and bicarbonate of the alkali by treatment with a solution of calcium bicarbonate in the cold. Schoch, however, failed to obtain any decomposition.

*Decomposition of Sodium Nitrate by Alumina.*—A mixture of nitrous vapours and oxygen is evolved, from which nitric acid is recovered in the usual way; the residue contains sodium aluminate, from which, by addition of carbonic acid, sodium carbonate is prepared and, simultaneously, alumina is recovered. The success of this reaction depends on the following conditions:—(1.) The complete decomposition of sodium nitrate. (2.) By far the greater portion of the nitric acid should be recovered. (3.) Too high a temperature combined with too long a duration of the operation is injurious. (4.) Vessels which are but little attacked should be used. Vessels of platinum, iron, or glass are too readily attacked, and Berlin porcelain can be used only for one operation.

*Decomposition of Calcium Sulphide by Calcium Chloride.*—Aarland (*ibid.*, **239**, 47) improved the Schaffner-Helbig sulphur-recovery process by substituting calcium chloride for the magnesium chloride used for decomposing the soda residues. Rickman, however, found (*Chem. Zeits.* 1880, 254) that on boiling fresh residues from the potash melt with a concentrated solution of calcium chloride decomposition could not be effected. Billitz has made a number of experiments with the view of deciding this point. He succeeded in decomposing the greater part



of the calcium sulphide by boiling with a large excess of calcium chloride for some time. He also found that on boiling calcium sulphide for about 55 hours with water *without* the addition of calcium chloride, more than half the calcium sulphide was decomposed. Calcium chloride therefore facilitates the decomposition.

*Preparation of Hydrochloric Acid from Calcium Chloride.*—Referring to Solvay's process of preparing hydrochloric acid by decomposing calcium chloride with superheated steam in presence of sand, clay, &c., the author gives the following particulars. On treating calcium chloride with more than 1 equivalent of silicic acid, 60·5, 66·8, 62·3, and 65·9 per cent. of hydrochloric acid was obtained in four experiments compared with the theoretical quantity of hydrochloric acid contained in calcium chloride. On treating calcium chloride with more than twice the weight of felspar, 66 per cent. of the theoretical quantity of hydrochloric acid was obtained; and on heating calcium chloride *per se* with steam to moderate redness, 54 per cent., and to bright redness, 60 per cent. of the theoretical quantity of hydrochloric acid contained in calcium chloride was obtained.

In conclusion, it is mentioned that hydrochloric acid prepared by Solvay according to the most recent improvements from calcium chloride, is too expensive to compete with hydrochloric acid obtained as a waste product in the preparation of sodium sulphate; in other words, that the ammonia-soda process, although possessing great advantages, cannot compete with the Leblanc process until the problem of a cheap mode of preparing hydrochloric acid from calcium chloride has been solved. D. B.

**Rule for Calculating the Composition of Glass, and on the Nature of Glass.** By G. WAGENER (*Dingl. polyt. J.*, 243, 66—70 and 152—156).—It is thought that a practical and trustworthy rule for calculating the ingredients necessary to form a good glass in presence of an indefinite proportion of lime and alkali would be much valued by glass manufacturers. According to the results of Weber (*ibid.*, 232, 350), good glasses are those which contain relatively the smallest amount of silicic acid. These will be found to correspond with the formula  $\text{CaO} + x(\text{Na}_2\text{O}, 6\text{SiO}_2)$  within a few per cent.: hence it follows that good glass should have a composition which would indicate that it formed a solution of lime in an indefinite (but sufficient) quantity of the silicate  $\text{Na}_2\text{O}, 6\text{SiO}_2$ . This silicate is capable of dissolving silicic acid: hence it follows, that on cooling, the presence of too large a quantity of lime, as well as silicic acid, would occasion crystallisation of the mass or devitrification. Although in the presence of an alkaline silicate with less than  $6\text{SiO}_2$  solution of the lime is effected, the resistance to chemical action nevertheless diminishes, and the glass becomes defective.

By disregarding the purely fractional rule demonstrated in the above, and proceeding from normal glass, the formula may be written thus:  $\text{Na}_2\text{O}, \text{CaO}, 6\text{SiO}_2 + (x - 1)(\text{Na}_2\text{O}, 6\text{SiO}_2)$  and  $x < \text{or} > 1$ . Although this formula agrees sufficiently well with Weber's tabulated results, more accurate numbers are obtained by a slight alteration, consisting in a small increase in the quantity of silicic acid. In the

case of  $x < 1$ , we obtain  $\text{Na}_2\text{O}, \text{CaO}, 6\text{SiO}_2 - (1 - x)(\text{Na}_2\text{O}, \frac{1}{2}\text{SiO}_2)$ , and for  $x > 1$ ,  $\text{Na}_2\text{O}, \text{CaO}, 6\text{SiO}_2 + (x - 1)(\text{Na}_2\text{O}, \frac{1}{2}\text{SiO}_2)$ .

In the second part the author discusses the nature of glass. The following is a summary of the conclusions arrived at:—Glass is the complete—that is, clear solidifying solution of one or more refractory substances in an alkaline silicate. In order to render glass capable of resisting the action of air, water, and acids, the solvent itself should resist their action, *i.e.*, it should form a strongly acid alkali silicate, and either should be present in sufficient quantity to surround and protect the dissolved body, or the latter should itself be capable of resisting atmospheric and other actions. D. B.

**Conversion Colours.** (*Dingl. polyt. J.*, **242**, 224.)—Balanche recommends the use of conversion colours in calico-printing. The principle of the first series of conversion colours treated consists in printing a mixture of two colours, one of these being destroyed by acids. After fixing the colours by steaming, an acid substance is printed on. Thus, two coloured patterns of pleasing effects may be produced. The following mixture is given as an example. 70 grams dark ultramarine, 5 grams dry lamp-black, 100 grams water, 50 grams gum tragacanth water (120 grams per litre), and 150 grams of egg albumin liquid (500 grams per litre). After printing and steaming, the following mordant is printed on: 50 grams acid potassium sulphate, 130 grams hot water. The dyed cloth is hung up in a moist room for 48 hours and passed through a bath of chalk at  $50^\circ$ . The ultramarine is destroyed at places where the acid salt has been deposited on the first printing colour, the lamp-black used remaining unaltered.

Instead of ultramarine blue, the green or red can be used, and the lamp-black replaced by any other pigment capable of resisting acids; thus a large number of combinations may be produced.

Balanche in a similar manner proposes to print on oiled goods a mixture of ultramarine, nitro-alizarin and albumin. After the destruction of the ultramarine, an orange colour is produced. By mixing ultramarine with alizarin, a violet is obtained, which is converted into a pink by destroying the ultramarine with an acid substance.

Balanche obtains a second series of conversion colours by replacing one mordant by another. By printing aluminium arsenate on alizarin purple, the aluminium takes the place of the iron at places where it comes in contact with the iron mordant of the alizarin, so that besides the unaltered parts of the purple, a pink colour is obtained. A similar effect is produced when uranium is used instead of iron, in which case a pink is produced beside a grey colour.

Balanche's third series of conversion colours is an application of steam colours. He prints alizarin on cloth with a quantity of aluminium acetate not sufficient to fix the colouring matter. The cloth is then passed through a rolling machine, and aluminium acetate printed on, so that at places where an excess of mordant has been deposited a darker shade is produced. D. B.

## General and Physical Chemistry.

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**Effect of the Spectrum on Haloïd Salts of Silver, and Mixtures of the Same.** By W. DE W. ABNEY (*Proc. Roy. Soc.*, **33**, 164—186).—The author alludes to the discrepant results hitherto obtained in investigations of the relative sensitiveness of the haloïd salts of silver in various parts of the spectrum, and to the importance of a more exact knowledge for the practical working of solar photography, and for a study of the laws of molecular physics. The apparatus employed was a two-prism spectroscope, and the sources of light were the sun and the crater of the positive pole of the electric light; the images from these sources were thrown on the slit by a condensing lens in the second case, and by the same and a heliostat in the first case. A long description is also given of the various vehicles for holding the sensitive salts, and the methods of printing, exposure, and development. From the diagrams given, it would appear that the curve of action of the spectrum on pure *silver iodide* begins beyond H, rises very gradually to a little beyond G, when it descends almost vertically; different times of exposure and methods of development make slight difference in the tail beyond H; but in few cases is there any action on the other side of G. With *silver bromide* the maximum action commences between G and F (nearer F than G), and the main differences in the impressed spectra lie in the tail on the least refrangible side. With *silver chloride* the maximum intensity is invariably reached between H and h, whether solar or electric light is used; according to some authors the maximum is near G, whilst according to others it is in the ultra-violet. With a mixture of silver iodide and bromide in equivalent proportions, free from silver nitrate, it appears that the subiodide formed combines with the liberated bromine to form silver iodobromide, while the subbromide combines with the iodine to form the same compound. The new molecule is most sensitive to the blue-green, and thus differs from either silver bromide or iodide taken separately. Similar reasoning and results apply to mixtures of silver chloride and iodide, but this mixture is less sensitive. Further researches are promised upon the organic sensitisers of the haloïds.

V. H. V.

**Electrolytic Diffusion of Liquids.** By G. GORE (*Proc. Roy. Soc.*, **33**, 140—143).—In a former communication, the author described various phenomena resulting from the passage of an electric current vertically through the boundary surfaces of two electrolytes lying upon each other; in the present paper he describes a form of apparatus employed to ascertain whether the mass of liquid expanded, or moved as a whole in the line of the current. The results of the experiments show conclusively that the liquid diffuses continuously downward through the boundary meniscus during the passage of the upward current; and secondly, as no manifest expansion occurs in the bulk of

the lighter of the electrolytes, equal volumes of liquid diffuse in opposite directions through the meniscus.

V. H. V.

**Some Effects of Transmitting Electric Currents through Magnetised Electrolytes.** By G. GORE (*Proc. Roy. Soc.*, **33**, 151—154).—This communication treats of a class of electro-magnetic rotations produced in liquids by means of axial electric currents, either in the interior of vertical magnets, electro or permanent, or near the poles of such magnets, and differ from rotations previously described, by the absence of radial currents. A column of an electrolyte inclosed in an electro-magnetic helix, is twisted in a similar manner to an iron wire or rod, placed under similar conditions.

The rotations produced in liquids are strongest at the poles, and a little distance beyond them, and *nil* at the centre. The rotations within the tube, and to a short distance beyond, are opposite to those produced by a voltaic solenoid; a magnet tube has then three points of rotation with an axial current, one at its centre, and one near each end, whilst a solenoid has only the former. These phenomena are more definite and powerful with a tubular electro-magnet than with a voltaic current alone.

V. H. V.

**The Constituent of the Atmosphere which absorbs Radiant Heat.** By S. A. HILL (*Proc. Roy. Soc.*, **33**, 216—226).—The author at the outset draws attention to the unsatisfactory conclusions drawn from laboratory experiments on the comparative diathermancy of dry air and water-vapour. In order to determine which constituent of the atmosphere has the greatest absorptive power, the author has collated a series of actinometric observations made at Dehra and Mussooree, in 1869 and 1879. The former of the stations is 2229 feet, the latter 6937 feet above the sea level. It is found that at Mussooree the values of solar radiation, computed according to Jamin's and Masson's law, were less than the values observed in the forenoon, but higher than those in the afternoon; while at Dehra there was no regular order in the differences. As these differences of heat absorption cannot be due to disturbances set up by heating from below, the increased absorption in the afternoon at Mussooree must arise from the fact that more of the absorbent substance lies above the level of the station in the afternoons than in the mornings. The absorbent substance is carried upwards during the day, and probably sinks down at night. But as the tension of aqueous vapour diminishes rapidly with the height above the sea level, it follows that a small variation in the quantity of it above the higher station will considerably affect the observed absorptive power. In other diagrams given in the paper it is shown that the variation of the absorption coefficient is similar in its chief features to that of the vapour-tension and of the humidity of the upper atmosphere as indicated by cloud, but differs totally from the variation of barometric pressure. The observations point strongly to the conclusion that water-vapour is the chief absorbent. This result agrees with those of Tyndall's laboratory experiments, and of Violle's observations in the Alps, which showed that the absorptive effect due

to water-vapour was about five times as great as that of perfectly dry air.  
V. H. V.

**Melting Points.** By E. J. MILLS (*Proc. Roy. Soc.*, **33**, 203—206).

—The author has devised a form of apparatus for the determination of melting points, which consists of an inverted glass funnel inserted in a bath; resting on the funnel is a thin test-tube filled with paraffin, in which are placed the thermometer bulb and capillary tube containing the substance whose melting point is to be determined. The advantage of this apparatus is the regular and constrained convection of heat, which cause a steady rise of the thermometer.

Attention is also drawn to the method of purification by *multiple successive solvents*, as recrystallisation from different solvents will often readily remove small quantities of impurities, which cling pertinaciously to substances, even when crystallised frequently from the same solvent. Certain relations between molecular weights and melting points are noticed, and examples are given which show how a series of isomerides may be identified by definite differences in their melting point.  
V. H. V.

**Refractive Power and Heat of Combustion.** By J. THOMSEN (*Ber.*, **15**, 66—67).—The author criticises and compares some of Brühl's (*Monatsh. f. Chem.*, 1881, 716) results, and comes to the conclusion that the qualitative alteration in the specific heat of combustion of a body by oxidation or substitution, is a perfectly useless foundation for a research on the connection between its optical and thermal properties.  
D. A. L.

### Heats of Combustion of some Members of the Fatty Series.

By W. LOUGUININE (*Ann. Chem. Phys.* [5], **25**, 140—144).

*Caproic Acid.*—Heat of combustion for 1 gram, 7156·97 cal.; for 1 gram-molecule, 830209 cals., a value differing by 2 per cent. from the number given by Favre and Silbermann. It is 5709 cal. lower than the heat of combustion of 2 mols. allyl alcohol, and 16939 cal. less than that of 2 mols. acetone.

*Octyl Alcohol* (b. p. 179·5).—Heat of combustion, for 1 gram, 9708·53 cal.; for 1 gram-molecule, 1262105 cals., a value less than 0·33 per cent. higher than that given by Favre and Zilbermann. The differences between the heats of combustion of the corresponding alcohols of the ethyl and allyl series are given in the following table:—

		Difference.
$C_3H_8O$ ....	480313 cals.	} 37663 cal.
$C_3H_6O$ .....	442650 "	
$C_4H_{10}O$ ....	636706 "	
$C_4H_8O$ ....	600128 "	} 36578 "
$C_5H_{12}O$ ....	793923 "	
$C_5H_{10}O$ ....	753214 "	} 40709 "
$C_6H_{18}O$ ....	1262105 "	
$C_6H_{16}O$ ....	1230040 "	} 32065 "
		2 q 2

The average difference is about 36800 cals., a number practically half the heat of combustion of  $H_2$ .

*Trimethyl Carbinol*.—Heat of combustion, for 1 gram, 8551.6 cals.; for 1 gram-molecule, 632818 cals. This number is not corrected for the heat of fusion, but closely approaches the value found by the author for isobutyl alcohol, and by Favre and Silbermann for butyl alcohol, thus affording further confirmation of the law that isomerides of the same chemical functions have practically the same heats of combustion.

*Pinacone*.—Heat of combustion for 1 gram, 7607.6 cals.; for 1 gram-molecule, 807697 cals. This value is not corrected for the heat of fusion of pinacone, but is of the same order as those of its homologues, ethylene glycol and isopropylene glycol. C. H. B.

**Flow of Gases and Properties of Flame.** By NEYRENEUF (*Ann. Chim. Phys.* [5], 25, 167—190).—The author has made a series of experimental verifications of Bernoulli's theorem on the flow of gases through small orifices. If the flow of gas takes place simultaneously through two orifices at different levels, the vertical distance between which is  $h$ , then the volume of gas issuing from the lower orifice is expressed by the formula (1)  $V^1 = \sqrt{2g \frac{b}{d}}$ , while that from

the higher is (2)  $V = \sqrt{\frac{2g}{d} b - h} (d-1)$ , ( $b$  = excess over atmospheric pressure at lower level;  $d$  = density of gas in terms of air). The value of  $V$  in the second formula becomes *nil* when  $b = h (d-1)$ , and if  $b < h (d-1)$  the value becomes imaginary; or in actual experiment the exterior air enters the higher orifice, until it reaches a distance  $h$  from the lower orifice, from which alone the flow of gas continues. If in formula (1)  $d > 1$ , then these conditions are reversed, and the flow of gas proceeds only from the upper orifice. This case can be realised by passing a continuous stream of carbonic anhydride into a Woulff's bottle, provided with three tubulures, one of which serves for the entrance of the gas, while the other two are equal in diameter and length, but at different levels serve for its exit. On regulating suitably the flow of gas, it is found that all the flow takes place through the lower tubulure. For cases in which  $d$  is a little less than 1, ordinary coal-gas may be used, when it is observed that the flame of gas from the lower tubulure is diminished in proportion as the gas delivery is decreased. Similar observations can be made with a Y-shaped tube with unequal branches, and so sensible is the form of apparatus, that the author proposes to substitute it for the ordinary spirit level; for differences of a length of a millimetre make a perceptible difference in the gas flame.

*Retrograde Flames*.—If  $a$  be the excess of pressure at the higher orifice, then if the pressure be so diminished that  $a - h (1-d) < 0$ , the air drives back the flame to the interior opening of the lower tubulures, so that two flames are produced, one within, and the other without the Woulff's bottle, and vibrations of the former cause synchronous pulsations of the latter, and an intense sound is the result.

If a light be applied only to the upper jet, and an influx of air is produced, the flame increases and diminishes in brightness in proportion as the gas is more or less rich in air. If the orifice be sufficiently narrow to prevent the combustion from passing into the interior of the vessel, the series of small detonations cause a musical flame similar to that of the chemical harmonicon of hydrogen.

*Sensitive Flames.*—By using an ordinary Bunsen burner, a sensitive flame may be produced in the following manner: if with a colourless flame the gas jet be gradually cut off until the flame is agitated with a sort of rotatory movement, and then the gas delivery is slightly diminished, the flame is divided into two portions, one exterior, long and dim, and the other interior, which rapidly heats the sides of the burner. Then any sharp sound drives down the exterior, and raises the interior flame, so as to produce a single flame while the sound lasts. The author has used this phenomenon to demonstrate the laws of reflection, refraction, and interference of sound. It is probable that the sonorous vibrations have an effect similar to those observed in the liquid veins of Savart's experiments.

*Flow of Gas in Pipes.*—The laws which regulate the flow of gas in rectilinear and cylindrical pipes have been studied by Girard, Graham, and others, but the ordinary methods of these experiments are very complex, and require numerous determinations of temperature and pressure. The author, by the use of the Y apparatus mentioned above, has verified these laws by photometrical observations, in which the variations of temperature and pressure can be practically neglected. For this purpose coal-gas, carefully freed from moisture, is passed into the Y-tube, the two branches of which are in communication with the tubes whose resistances are to be compared, each of which is furnished with a suitable jet. Then the flames at the two jets, placed exactly at the same level, will be equal in intensity when the resistances of the tubes are equal. In this way the author has confirmed the laws of Girard and Poiseuille for tubes of large and small diameter.

*Properties of Flames.*—A flame burning at a jet produces two opposite effects, one an onward flow of gas, caused by the current of the surrounding heated products of combustion, and the other a backward flow, due to their expansion. Either of these effects can be rendered predominant by an alteration of the size of the orifice; for conical flames the latter, but for cylindrical and forked flames the former is predominant. If by means of the Woulff's bottle with three tubulures alluded to above two equal flames are produced, and one of them is surrounded by a chimney, then its flame is elevated; but if the experiment be so modified that sonorous vibrations are produced, then the flame not surrounded by the tube is elevated, for the vibratory movements decrease the delivery, but increase the internal pressure of the gas. If the speed of flow be diminished without any modification of the combustion, a result which may be attained with a horizontal cylindrical flame issuing from a large aperture, a bass sound is frequently produced, and accompanied by a partition of the flame into two longitudinal fissures. But the most efficacious method of obtaining sonorous flames is by the impact of two flames, a treble sound being produced when the impact takes place at the lower portion, but

a bass sound if at the centre of the flames. Similar relations are caused by the impact of the gas against a solid body, or by passing the gas through a very small orifice, or by the introduction into the burner of a screw-shaped piece of iron. By the impact of two flames, of which one issues from an irregular opening, sympathetic flames are produced, which will reproduce either a series of sounds, as the gamut, or even a musical tune. These experiments are also analogous to those of Savart on "liquid veins." V. H. V.

**Coefficients of Contraction and Expansion of Silver and Cuprous Iodides and their Alloys.** By G. F. RODWELL (*Proc. Roy. Soc.*, 33, 143—145).—The author has prepared and determined the physical and chemical properties of alloys of silver and cuprous iodides, which contained from 38—88 per cent. of silver iodide.

The following are the principal facts noticed:—(1.) The sp. gr. varies from 5.73 to 5.69, and is little above the mean sp. gr. of the constituents; (2), the melting point varies from 514° to 493°, which is considerably lower than the melting point of silver or cuprous iodide. (3.) Some of the alloys possess three points of similar density, and some, two, at different temperatures; they are resinous, and transparent in thin layers; when pulverised they appear as brilliant yellow powders; (4), the coefficients of expansion of the alloys below the point at which contraction commences, decrease as the percentage of silver iodide increases. (5.) The temperature at which this contraction commences is lowered with decrease of silver iodide: it varies from 284° to 153°. The structure and properties of these alloys are also compared with those of the lead-silver iodide and copper-silver iodide alloys, which the author has previously described (*comp. Abstracts*, 1881, 495, 965, &c.). V. H. V.

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### Inorganic Chemistry.

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**Silicon.** By P. SCHÜTZENBERGER and A. COLSON (*Compt. rend.*, **93**, 1508—1511).—When crystallised silicon is heated almost to whiteness in a porcelain tube in an atmosphere of carbonic anhydride, the latter is absorbed, with formation of a greenish-white mass, which may be freed from silicon by washing with hot moderately concentrated potash. The residue is then treated with hydrofluoric acid, which dissolves out silica, leaving a greenish powder, insoluble in boiling solutions of the alkalis, and not attacked by any acids. It has the composition  $x\text{SiCO}$ , and is formed in accordance with the equation  $\text{Si}_3 + 2\text{CO}_2 = \text{SiO}_2 + 2\text{SiCO}$ . When heated in oxygen, it yields only a trace of carbonic anhydride, but is oxidised with incandescence when heated with litharge or a mixture of litharge and lead chromate.

When crystallised silicon is heated to whiteness in a brasqued crucible, as in Wöhler's experiment, the mass, after washing with boiling potash to remove silicon, and treatment with hydrofluoric acid to

remove silica and silicon nitride, yields a bluish-green, pulverulent residue, insoluble in alkalis and in all acids. Heated to redness in oxygen or with cupric oxide, it undergoes no sensible change, but when heated with litharge, lead dioxide, or a mixture of litharge and lead chromate, it burns brilliantly, with formation of oxides of nitrogen and carbonic anhydride. It has the composition  $\text{Si}_2\text{C}_2\text{N}$ . The existence of the two similar compounds  $\text{Si}_2\text{C}_2\text{O}_2$  and  $\text{Si}_2\text{C}_2\text{N}$  indicates the existence of a tetrad radicle *carbosilicon*  $\text{Si}_2\text{C}_2$ , which forms a dioxide and a nitride analogous respectively to carbonic anhydride and cyanogen. The carbonitride is formed whenever crystallised silicon is heated in a current of cyanogen, or with carbon or a carbonaceous substance in an atmosphere of nitrogen.

By heating crystallised silicon to bright redness in a porcelain tube, in an atmosphere of pure nitrogen, a white mass is obtained, which, after treatment with potash and hydrofluoric acid, yields an insoluble residue of the composition  $\text{Si}_2\text{N}_3$ . If the product of the action of dry ammonia on silicon tetrachloride is heated to redness in a current of hydrogen, a white powder is obtained of the composition  $\text{Si}_2\text{N}_6\text{Cl}_3$ . When this is heated to redness in a current of ammonia, all the chlorine is expelled in the form of hydrochloric acid, and the compound  $\text{Si}_2\text{N}_3\text{H}$  is formed. This dissolves rapidly in caustic alkalis with evolution of ammonia, and is also soluble in hydrofluoric acid, the nitrogen being converted into ammonia. These facts would indicate the existence of a monatomic radicle  $\text{Si}_2\text{N}_3$ .

The compound  $\text{Si}_5\text{N}_6\text{Cl}_2$  has probably the constitution  $\text{SiCl}_2 < \begin{matrix} \text{Si}_2\text{N}_3 \\ \text{Si}_2\text{N}_3 \end{matrix}$ ,  
C. B.

**Crystallisation of Silica from Fused Metals.** By R. S. MARSDEN (*Proc. Roy. Soc. Edin.*, **11**, 37—40).—When some silver and carbon were fused in Berlin porcelain crucibles, the silica of the glaze of the crucibles was absorbed into the silver, from which it was separated by nitric acid in the usual hexagonal crystals, and also in a leaf-like form.  
E. W. P.

**Compounds of some Solid Hydrated Dioxides with Acids, Salts, and Alkalis.** By J. W. v. BEMMELEN (*J. pr. Chem.* [2], **23**, 324—349, 379—395).—This is an account of a series of experiments, the object of which is to show that the absorptive power of certain hydrated dioxides for acids, salts, and alkalis, is due to a species of chemical action. The author has experimented with hydrated forms of silicon dioxide, metastannic acid, stannic acid, and the red and black variety of manganese dioxide. (For an account of the preparation and composition of these, see this Journal, **38**, 849.) The following acids and salts contained in solutions of known strength were used:— $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{KNO}_3$ , and  $\text{KCl}$ . In these experiments a given weight of the oxide was shaken up with a known volume of the solution, and the solutions were analysed afterwards. Silica, with 4 mols. of water of hydration, was found to absorb these acids and salts, within certain limits of concentration, in quantities proportional to the concentration and the water of hydration of the silica. In the case of the other hydrated oxides, the absorption is greater than that

corresponding with the water of hydration or the concentration of the solution. Metastannic acid ( $\text{SnO}_2 \cdot 2\cdot3\text{H}_2\text{O}$ ) was found to combine with larger quantities of acids than of salts, and from the latter, with sulphates more than with nitrates or chlorides. After drying at  $100^\circ$ , becoming ( $\text{SnO}_2 \cdot 1\cdot2\text{H}_2\text{O}$ ), it loses its absorptive power to some extent. The phenomena exhibited by hydrated manganese dioxide are of special interest; the red variety combines more readily with sulphuric acid than does the black; both combine with the salts, and in some cases are capable of decomposing small quantities of the salts, liberating the acid and combining with the alkali. This decomposition is more complete when the solutions are dilute, and serves to explain the observations of Gorgeu (*Ann. Chim. Phys.* [3], 66), that solutions of salts of alkalis and alkaline earths become acid when brought in contact with manganese dioxide. These oxides absorb potash from its solutions; silica combines with large quantities, forming soluble compounds, as does metastannic acid. The amount of potash absorbed by manganese dioxide is dependent on the concentration of the solution, which may explain the fact that many chemists have been unable to obtain constant numbers in the analysis of hydrated manganese dioxide, inasmuch as they were experimenting with dissociation products, which are decomposed by washing.

The author has also observed that the salts, &c., absorbed by an oxide, may be replaced by others, *e.g.*, sulphuric acid retained by manganese dioxide, may be removed by treatment with a solution of potassium sulphate. Similarly, sulphuric acid, held by metastannic acid, may be expelled by nitric acid.

The fact that such substances as titanous acid and manganese dioxide, in the finely divided state, when suspended in water, may be made to cohere when treated with an acid or a salt solution, is to be attributed to a combination and consequent formation of molecular aggregations, which depend for their existence upon the concentration of the solution. By dilution, these aggregations are destroyed, and the oxide passes once more into the finely divided state. P. P. B.

**Oxidation of Ferrous Salts.** By J. Y. BUCHANAN (*Proc. Roy. Soc. Edin.*, 11, 191—198).—In this interesting paper it is shown that the present ideas concerning the influence of the presence of oxidising agents on a solution of ferrous salt, are very erroneous. Three solutions of ferrous sulphate were prepared; of the first 10 c.c. contained 0.0407 gram Fe; of the second, 10 c.c. contained 0.062 gram Fe; and of the third, 10 c.c. contained 0.1 gram Fe; of the potassium chlorate solution 10 c.c. contained sufficient chlorate to oxidise 0.1 gram Fe from the ferrous to the ferric state. Solutions of potassium nitrate and permanganate with sulphuric and hydrochloric acids were employed. It is generally supposed that titration with permanganate, in presence of strong hydrochloric acid, cannot be accomplished correctly, but the author shows that it is perfectly possible to obtain correct results, if the permanganate is added so as to avoid local supersaturation, as all the iron is oxidised before any euchlorine is formed, and the point of completion can be indicated by the addition of a little potassium ferricyanide, so as to produce a blue coloration only, which disappears

directly all ferrous salt is oxidised. The table of experimental results shows that, with addition of 10 c.c. of fuming hydrochloric acid, as good results were obtained as when sulphuric acid was employed. The presence of potassium chlorate or perchlorate does not affect immediately the results at ordinary temperatures. Also at ordinary temperatures, neither potassium perchlorate nor nitrate has any appreciable effect, although allowed to be in contact for several hours, whilst it is only after the lapse of an hour that the chlorate acts on the ferrous salt. At the boiling point, nitrates and perchlorates are not detrimental; but not so the chlorate. Dilution of the chlorate solution reduces its influence, for below 7 per cent. it seems to have no effect.

E. W. P.

**Arsenical Bismuth Subnitrate.** By R. H. CHITTENDEN and S. W. LAMBERT (*Amer. Chem. J.*, **3**, 396—402).—The frequent occurrence of arsenic in commercial bismuth subnitrate, previously noticed by Taylor and others, has been confirmed by the authors of the present paper; out of fourteen samples analysed, only one was found to be quite free from arsenic, whilst the average amount was found to be 0.013 per cent. or 13 mgm.  $\text{As}_2\text{O}_3$  in 100 grams of the subnitrate. In one sample, 100 grams were found to contain 77 mgm., or 1.2 grains of arsenious oxide, which is about half a fatal dose of the poison.

With regard to the retention of arsenic in the animal organism, the authors observe that arsenic is not necessarily an accumulative poison: for though it may accumulate for a time in certain organs or tissues, elimination soon commences; and if all the excretory organs are in normal condition, it is very doubtful whether there can be any great retention of the poison, when only small quantities are taken at somewhat distant intervals. To determine whether elimination of arsenic goes on at the same rate as its absorption, experiments were made upon a large healthy dog, to which arsenical bismuth subnitrate containing 0.01226 per cent. arsenic was given in his food in gradually increasing doses. This treatment was continued for 39 days, at the end of which time the dog was killed, and the various organs and tissues were examined for arsenic. The experiment showed that the greater part of the arsenic had not been absorbed—a result probably due to the fact that the arsenic in bismuth subnitrate is present in the form of a compound only very slightly soluble in water. This was indeed directly proved by repeatedly drenching a sample of arsenical bismuth subnitrate with water, and examining the filtered liquid for arsenic by Marsh's test, the results being that not a trace of arsenic was found in the liquid. It may therefore be concluded that although medicinal bismuth subnitrate usually contains a weighable quantity of arsenic, the poison is not present in a form in which it is readily absorbed by the animal organism. This fact, however, does not lessen the desirability of possessing a preparation of bismuth entirely free from arsenic.

H. W.

## Mineralogical Chemistry.

**Crystallogenic Observations.** By V. FOULLON (*Jahrb. f. Min.*, 1882, 1, Ref., 349).—The author describes the mode of growth of the crystals of magnesium sulphate and sodium chlorate in solutions to which another salt has been added. Magnesium sulphate very often crystallises from a pure solution entirely without hemihedral forms; but the crystals of the same salt which separate from a solution also containing borax, are decidedly hemihedral, and as they go on growing in the same solution, the faces of the pyramids become covered with flat conical elevations, which, after some time, grow into small crystals, the orientation of which is not in accordance with that of the principal crystal.

The addition of sodium sulphate to a solution of sodium chlorate, gives rise to the predominance of a tetrahedron on the crystals which separate therefrom.

Crystals of alum exhibiting the combination  $O.\infty O\infty$ , when immersed in a solution of the same salt made alkaline with sodium carbonate, were found to be attacked with different degrees of rapidity on the dissimilar faces, the octohedral faces, after a few days, being considerably depressed by etch-figures, whereas the cube-faces retained their lustre, and exhibited only a few isolated etch-figures. H. W.

**Mineralogical Notices.** By C. VRBA (*Zeitschr. f. Kryst.*, 5, 417; *Jahrb. f. Min.*, 1882, 1, Ref., 355—359).—1. *Anatase from Rauris in Salzburg.* Small crystals, implanted, together with adularia, quartz, and distinct chlorite-crystals, on gneiss partly coated with ferric hydroxide. They exhibit the forms  $0P$ ,  $P$ ,  $\frac{1}{2}P\infty$ ,  $\frac{1}{6}P$ ,  $\frac{1}{3}P$ ,  $\infty P$ . Tabular development according to  $0P$  with  $P$  or  $\frac{1}{2}P\infty$  predominant. Angle  $\frac{1}{3}P\infty : 0P = 149^\circ 21\frac{1}{2}'$ ;  $\frac{1}{3}P\infty : P = 130^\circ 47\frac{1}{2}'$ .

2. *Stephanite from Pribram.*—Orthorhombic, exhibiting the faces  $\infty P\infty$ ,  $\infty P\infty$ ,  $0P$ ,  $\infty P\bar{5}$ ,  $\infty P\bar{3}$ ,  $\infty P\bar{2}$ ,  $\infty P$ ,  $\infty P\bar{3}$ ,  $P\infty$ ,  $2P\infty$ ,  $\frac{2}{3}P\infty$ ,  $P\infty$ ,  $\frac{4}{3}P\infty$ ,  $\frac{2}{3}P\infty$ ,  $2P\infty$ ,  $4P\infty$ ,  $\frac{1}{3}P$ ,  $\frac{1}{2}P$ ,  $P$ ,  $\frac{5}{2}P\bar{5}$ ,  $5P\bar{5}$ ,  $\frac{3}{4}P\bar{3}$ ,  $3P\bar{3}$ ,  $7P\frac{1}{3}$ ,  $4P\bar{2}$ ,  $P\frac{5}{3}$ ,  $\frac{5}{2}P\frac{5}{3}$ ,  $2P\bar{2}$ ,  $3P\bar{3}$ ,  $\frac{5}{2}P\bar{5}$ . Either the pyramidal and dome-faces predominate in the combination, or the crystals are short or long prismatic. Sp. gr. = 6.271. Analysis gave 15.61 per cent. S, 16.48 Sb, 67.81 Ag, with traces of copper and iron. Total 99.90.

3. *Datolite from Theiss in Tyrol.*—Two intergrown spherules of chalcedony are found in this locality, both lined with quartz-crystals, on which are implanted in the one spherule a few crystals of comptonite, in the other much distorted crystals of datolite. Between the latter is deposited a yellowish, soft, earthy substance, enclosing small perfectly developed crystals of datolite, exhibiting the faces —  $P\infty$ ,  $0P$ ,  $P\infty$ ,  $2P\infty$ ,  $\infty P\infty$ ,  $P$ ,  $\infty P\bar{2}$ , —  $2P$ , —  $P\bar{2}$ ,  $3P\bar{6}$ , the last having been previously observed only on datolite crystals from Arendal. The small crystals are tabular, according to —  $P\infty$ , colourless, transparent, with tolerably flat faces and good reflection.

4. *Frieseite from Joachimsthal.*—A few small crystals of this mineral, extracted from a geode of argentopyrite, exhibited, in addition to the pre-

viously known forms,  $0P$ ,  $\infty P\infty$ ,  $\frac{1}{2}P\infty$ ,  $3P\infty$ , also the following:  $P\infty$ ,  $\frac{4}{3}P\infty$ ,  $3P\frac{2}{3}$ . The development of the crystals is tabular in the direction of the base, and elongated in that of the macrodiagonal. The crystals occur regularly intergrown with those of argentopyrite, the two minerals intersecting one another in such a manner that the two halves of a frieseite tablet are sometimes implanted on the two sides of a crystal of argentopyrite, while in other cases the opposite arrangement is observed.

5. *Pseudomorphs of Iron Pyrites from Pribram.*—These pseudomorphs are implanted, together with crystals of iron-pyrites—sometimes also upon these—on a layer of galena covered with a crust of quartz, the galena also covering a layer of ferrous carbonate, 2 to 3 cm. thick. Some of the crystals are tablets, mostly hexagonal, of the thickness of paper, and either single or arranged in cellular or fan-shaped groups. In one instance only was a triangular striation observed on the basal face. By this observation, together with the earlier statements of Reuss and Blum, the author was led to regard the iron pyrites as a pseudomorph after polybasite. Analysis gave 37.50 per cent. Fe; 43.74 S, 2.50 Pb, 5.20 Mo, 5.40  $\text{CaCO}_3$ , 3.71  $\text{SiO}_2$ , 0.41 Ag, and a trace of copper (= 98.46); numbers which, after deduction of quartz, calcium carbonate, and lead molybdate—which is implanted on the pseudomorphs in the form of minute crystals of wulfonite—leads very nearly to the formula of iron bisulphide; analysis 46.16 per cent. Fe, 53.84 S; calc. 46.67 Fe, 53.33 S. Some of the pseudomorphs in the Clementi vein form rosettes of rather large six-sided tablets, surrounded by a crust of pyrites, and formed internally of variously coloured zones, resembling the pseudomorphs of marcasite after magnetic pyrites from Waldenstein and Loben in Carinthia, and have perhaps been formed from the same mineral. In this locality, however, there also occur, together with heavy spar, dark-coloured very efflorescent tablets, probably consisting of marcasite and formed after niargyrite.

6. *Emerald from Santa Fé di Bogota.*—The author examined two crystals from this locality, one of a very fine green colour and transparent, the other less brightly coloured and less transparent. Only a few of the forms occurring on these crystals are present with all their faces; and many of them had previously been observed only on beryl; others not even on that mineral. In the following enumeration, the new faces are distinguished by stars:— $0P$ ,  $\infty P$ ,  $\infty P2$ ,  $\frac{1}{2}P$ ,  $P$ ,  $\frac{3}{2}P$ ,  $2P$ ,  $3P^*$ ,  $4P^*$ ,  $12P^*$ ,  $\frac{2}{3}P2^*$ ,  $2P2$ ,  $6P2^*$ ,  $P\frac{3}{2}$ ,  $2P\frac{3}{2}$ ,  $3P\frac{3}{2}$ ,  $24P\frac{3}{2}$ ,  $\frac{6}{5}P\frac{6}{5}^*$ . The following measured angles between the new faces and the faces  $0P$  and  $\infty P$  agree very nearly with the theoretical values;  $3P : 0P = 119^\circ 37'$ ;  $4P : 0P = 113^\circ 9'$ ;  $12P : 0P = 98^\circ 12'$ ;  $\frac{2}{3}P2 : 0P = 161^\circ 31'$ ;  $6P2 : 0P = 108^\circ 38'$ ;  $\frac{6}{5}P\frac{6}{5} : \infty P = 109^\circ 59'$ . H. W.

**Beegerite, a New Mineral.** By G. A. KÖNIG (*Jahrb. f. Min.*, 1882, 1, Ref., 365).—A sulphide of lead and bismuth, found in small crystals, together with quartz, on the Baltic vein of the Geneva Mining Company, at Grant Post Office, Park County, Colorado. At first sight, it appears to be rhombic, but it is really a regular combination of the cube and octohedron, elongated in the direction of an octohedral edge.

Cleavage very distinct, parallel to the cubic faces. Sp. gr. = 7.273. Heated in a flask, it decrepitates, and melts at a red heat without subliming. Heated in an open tube, it gives off sulphur dioxide, and at a strong heat traces of a white sublimate (antimony). On charcoal in the oxidising flame, it melts to a globule, yielding a yellow deposit of lead and bismuth. The residue gives with borax a faint copper reaction. The fine powder is slowly dissolved by hydrochloric acid at ordinary temperatures, with evolution of hydrogen sulphide; very quickly on heating. Analysis: 64.23 per cent. Pb, 20.59 Bi, 14.97 S, and 1.70 Cu = 101.49, leading to the formula  $\text{Pb}_5\text{Bi}_2\text{S}_9 = 6\text{PbS}, \text{Bi}_2\text{S}_3$ . Allied to this mineral are cosalite,  $(\text{PbAg})_2\text{Bi}_2\text{S}_3$ , and schirmerite,  $(\text{PbAg}_2)_3\text{Bi}_4\text{S}_9$ , the latter from the Treasury-vein of the same mine.

H. W.

### Artificial Pseudomorphs of Göthite, Limonite, and Hæmatite.

By G. KELLER (*Jahrb. f. Min.*, 1882, 1, Ref., 363).—The author prepared pseudomorphs of ferric hydroxide after iron pyrites, by pulverising the latter in such a manner that crystal-faces remained visible here and there; then collected it on a filter, and left it for ten weeks, drenching it three times a week with a little water containing in solution acid carbonate of calcium. The filtrate was found to contain sulphuric acid, and each individual grain of the pyrites became coated with a thin yellowish-brown crust of ferric hydroxide, preserving, however, its form unaltered. Pure water exerted on iron pyrites merely an oxidising and dissolving action.

The author has also imitated artificially the process by which pseudomorphs of limonite after calcite are formed in the beds of magnetic pyrites at Bodenmais, viz., by immersing a lump of calcite for twelve weeks in a solution of ferric sulphate. The calcite then became covered with a crust of ferric hydroxide, retaining its own form. When dried in an oven, the hydroxide lost its water, and was converted into brown-red ferric oxide (hæmatite).

H. W.

### A probably Dimorphous Form of Tin, and some Crystals found associated with it.

By C. O. TRECHMANN (*Min. Mag.*, 1879, 3, 186; *Jahrb. f. Min.*, 1882, 1, Ref., 359). **On Crystallised Tin.** By H. v. FOULLON (*Jahrb. f. Min.*, loc. cit.).—In cavities of the so-called "hard head," a scoriaceous mass rich in arsenic, which is precipitated at certain stages of the smelting of tin,—sometimes also in the ordinary slag, e.g., at the Chyandour Works near Penzance,—crystals are found containing, according to analyses by J. W. Collins, 98.5 to 98.7 per cent. tin. 1.0 to 1.1 iron, and traces of cobalt, sulphur, and arsenic, and differing in form from the tin-crystals obtained by electrolysis, which belong to the quadratic system. They occur as a loose aggregate, or implanted on the slag singly or in groups, and have the form of six-sided plates only 6 mm. long, and often built up of sub-individuals, in such a manner as to produce a figure toothed like a comb. The ordinary quadratic form of tin may be distinguished as  $\alpha$ -, the new form as  $\beta$ -tin. The latter is orthorhombic, with the axial ratio  $a : b : c = 0.3874 : 1 : 1.03558$ ; in  $\alpha$ -tin, according to Miller,  $a : c = 1 : 0.3857$ . Observed forms of  $\beta$ -tin:  $\infty\text{P}\infty$ ,  $\infty\text{P}\infty$ ,  $\infty\text{P}$ ,  $\infty\text{P}\bar{2}$ ,  $\text{P}$ ,  $\text{P}\infty$ ,  $2\text{P}\infty$ . In the crystals of  $\alpha$ -tin,  $0\text{P} : \text{P}\infty = 158^\circ 54' 5''$ ;

$0P : 3P\infty = 130^\circ 50'$ ; in those of  $\beta$ -tin,  $\infty P\infty : \infty P = 158^\circ 49'5''$ :  
 $\infty P\infty : P\infty = 132^\circ 34'$ .

The two forms of tin exhibit a close morphological relation, but their other physical properties show that they are not identical.  $\beta$ -tin has a dark iron-grey to graphite-grey colour, strong metallic lustre, and shining iron-grey streak; it is brittle, but somewhat ductile under pressure; cleaves very imperfectly parallel to  $\infty P\infty$  and  $P\infty$ . Sp. gr. = 6.525 to 6.557, probably too low from admixture of the crystals next to be described.

Among these crystals of  $\beta$ -tin, there occur a few very small orthorhombic crystals, hard and brittle, with a light iron-grey colour and strong metallic lustre, probably consisting of a tin-compound containing iron. Observed faces  $\infty P\infty$ ,  $\infty P\infty$ ,  $\infty P$ ,  $P\infty$ . Axes  $a : b : c = 0.9018 : 1 : 0.5652$ .

Tin-crystals from the smelting furnaces of the Graupen Tin Works at Mariaschein have lately been described by H. v. Foullon. They are of two kinds, the one extremely small, corroded, faintly lustrous, and covered with a thin metallic film; the others considerably larger, measuring from 1 to 10 mm., tabular parallel to  $\infty P\infty$ , strongly lustrous, much corroded, and exhibiting a fine laminated structure. The crystals of both kinds, as well as the metallic walls to which they adhere, contain, besides tin, only traces of iron, copper, and carbon. They exhibit all the faces above enumerated except  $\infty P\infty$  and  $2P\infty$ ; also two new faces  $\infty P\frac{1}{2}$  and  $2P\frac{1}{2}$ . H. W.

**Glauberite, &c.** By E. PFEIFFER (*Arch. Pharm.* [3], 19, 430—433).—A description of minerals found in sinking the Douglasshall shafts. A layer of glauberite, ( $\text{Na}_2\text{SO}_4, \text{CaSO}_4$ ), a meter thick was met with. A bright green rock-salt was also found containing, according to Ochsenius, 3.5 per cent. ferrous chloride and 7.88 per cent. potassium chloride. Precht, however, found 59 per cent. potassium chloride and 41 per cent. sodium chloride with crystals of potassio-ferrous chloride, ( $2\text{KCl}, \text{FeCl}_2, 2\text{H}_2\text{O}$ ), inclosed, for which salt Ochsenius proposed the name of douglasite. Ferrous chloride was also found in boracite; and in tachhydrite both ferrous and ferric chlorides were found.

As large quantities of combustible gases are met with in starting new potassium works, Precht suggests that the hydrogen which they contain may be due to the decomposition of water by ferrous chloride. Precht found in 100 mols. of such a gas—

H.	$\text{CH}_4$ .	N.	$\text{CO}_2$ .	O.	CO.
93.053	0.778	5.804	0.180	0.185	trace

F. L. T.

**Jarosite from a New Locality.** By G. A. KÖNIG (*Zeitschr. f. Kryst.*, 5, 317; *Jahrb. f. Min.*, 1882, 1, Ref., 363).—This mineral is found in silver ore in the porphyry, 6 miles east and 2 miles north of South Arkansas, and about 600 feet above the River Arkansas, in Chaffee County, Colorado. The material consists wholly of crystals and crystalline groups. The former exhibit the faces R and OR. Terminal edge-angle of R =  $89^\circ 15'$ ; R : OR =  $124^\circ 45'$ . Axial ratio



$a : c = 1 : 1.250$ . Lustre on the crystal-faces, adamantine; on the fracture, resinous. Colour, deep brown, seldom yellow on the crystals, more frequently on the crusts. Perfectly transparent. Streak-powder light yellow. Sp. gr. = 3.144 (not quite exact, on account of admixed quartz and thurgite). An analysis gave—

$\text{Fe}_2\text{O}_3$ .	$\text{K}_2\text{O}$ .	$\text{Na}_2\text{O}$ .	$\text{SO}_3$ .	$\text{H}_2\text{O}$ .
52.36	7.36	0.90	29.33	10.55 = 100.50

leading to the formula  $\text{K}_2\text{Fe}_6\text{S}_4\text{O}_{22} + 6\text{H}_2\text{O}$ . Another analysis gave somewhat different results. Part of the iron is calculated as thurgite,  $\text{Fe}_2\text{H}_2\text{O}_7$ , for the quantity of which, however, there are no exact data available. The author regards jarosite as a distinct mineral species resembling alunite in form and composition, and different from the potash-copperas or Gelbeisenerz of Bohemia.

H. W.

**Cyprusite, a New Mineral.** By P. F. REINSCH (*Proc. Roy. Soc.*, **33**, 119—121).—In a not much explored part of Cyprus near Chrysohu Bay, the author found a remarkable mineral, composed principally of ferric sulphate. It covers the sides of a hill, and forms compact, prominent rocks of 1 to 2 meters high. It is partially soluble, and the neighbouring ravines are covered with efflorescent crusts of ferrous sulphate, which probably increase after each rainy season. The residue, insoluble in hydrochloric acid, consists of well-preserved shells of microscopic radiolaria of different genera. The following is the composition of cyprusite:—

Ferric oxide with alumina.....	51.5
Sulphuric acid.....	21.5
Residue insoluble in HCl(silica, &c.) ..	25.0
Water .....	2.0
	<hr/>
	100.0

V. H. V.

**A New Manganese Mineral.** By M. W. ILES (*Amer. Chem. J.*, **3**, 420—422).—This mineral occurs in Hall Valley, Park Co., Colorado, in a quartzose rock containing the sulphides of iron, lead, and zinc. It is composed of loosely adherent, very friable, thick orthorhombic (?) prisms, frequently terminating in truncated pyramids.  $H = 0.75$  to 1. Sp. gr. = 2.167. Lustre, slightly glimmering. Colour, milk-white, sometimes stained with ferric oxide. Taste bitter, astringent. Very soluble in water even at the ordinary temperature; the solution effervesces with sodium carbonate, blues litmus paper, and gives a very slight iron precipitate on boiling; no coloration with ammonium thiocyanate. Analysis gave as mean result—

$\text{MnO}$ .	$\text{FeO}$ .	$\text{ZnO}$ .	$\text{SO}_3$ .	$\text{H}_2\text{O}$ .
22.31	4.18	5.97	36.07	31.60 = 100.13,

agreeing nearly with the formula  $5\text{MnSO}_4, \text{FeSO}_4, \text{ZnSO}_4, 28\text{H}_2\text{O}$ . The mineral exhibits a close resemblance to Fausserite,



H. W.

**The Pegmatite Veins of Moos and the Minerals contained in them.** By W. C. BRÖGGER (*Jahrb. f. Min.*, 1882, 1, Ref., 349—352).—The Peninsula of Aanneröd (about 6 km. east of Moos), consisting of gneiss and crystalline slates, is extraordinarily rich in coarse-grained granite-veins, the thinner of which have no determinate direction, whereas the thicker veins conform to the dip of the slates, and run nearly parallel to them. Although they are of similar origin and are united by transition-strata, nevertheless two types may be clearly distinguished, the thicker and more frequently occurring veins being especially characterised by orthoclase (including microcline) and magnesia mica; the others by plagioclase (oligoclase, albite) and potash-mica. The former contain also large quantities of quartz, together with oligoclase, potash-mica, albite, garnet, magnetite and occasionally monazite, apatite, aannerödite; whereas the latter are less rich in quartz, contain but very little orthoclase, and, as accessory minerals, chiefly beryl, garnet, topaz, and likewise aannerödite. According to Brögger, the same types may be recognised in many other localities, e.g., at Arendal, Hitteroe, Itterby, Brodbo, Finbo, Haddam, Adelaide, and Allebaschka.

Besides the minerals just mentioned, tourmalin occurs as an accessory constituent, and especially on druses, iron pyrites, albite, fluor-spar and quartz.

The new mineral, aannerödite, exhibits the following properties:—Colour black. Streak brownish or greenish-grey, according to the freshness of the mineral. Opaque to brownish-translucent on the edges. Lustre faintly metallic to fatty-semimetallic. Brittle. Fracture imperfectly conchoidal. No distinct cleavage. H. = 6. Sp. gr. = 5·7. Melts with difficulty before the blowpipe to a black glass. The crystals are often grown together in bundles of parallel fibres, or radially grouped. The mineral usually occurs imbedded in magnesia mica. An analysis by C. Blomstrand gave:—

Nicbie oxide .....	48·13	Manganous oxide .....	0·20
Stannic oxide .....	0·16	Lime.....	3·35
Silica .....	2·51	Magnesia.....	0·15
Zirconia (impure) .....	1·97	Potash .....	0·16
Uranous oxide.....	16·28	Soda.....	0·32
Thorina .....	2·37	Alumina .....	0·28
Cerium oxides.....	2·56	Water .....	8·19
Yttrium oxides .....	7·10		
Lead oxide .....	2·40		99·51
Ferrous oxide .....	3·38		

Hence Blomstrand—regarding the silica as accessory—calculates the formula  $2R_2Nb_2O_7 + 5Aq$ ; according to which the new mineral differs from samarskite and noblite only in the amount of water. Brögger, on the other hand, regards the water in aannerödite as well as in noblite as only a secondary constituent, inasmuch as its amount is very variable (some specimens being nearly anhydrous), and the physical properties of the mineral vary regularly according to the amount of water contained in it. From samarskite (Mitchel Co.), on the contrary, aannerödite differs in its crystallographic similarity to

columbite. Axial ratio  $a : b : c = 0.40369 : 1 : 0.36103$ . Observed faces  $P$ ,  $\infty P$ ,  $\infty P\infty$ ,  $2P\infty$ ,  $\infty P\infty$ ,  $\infty P\infty$ ,  $0P$ ,  $\frac{1}{2}P\infty$ ,  $P\infty$ ,  $2P\infty$ ,  $2P\infty$ ,  $3P\infty$ ,  $2P$ . The principal types are (1) long prismatic, like those of polycrase; (2) vertically tabular according to  $\infty P\infty$ , sometimes short, sometimes long; (3) crystals resembling quadratic prisms by the equal development of the two pinacoids; (4) short prismatic with monosymmetric habit. To these must also be added an intersection twin according to  $\infty P\infty$ . H. W.

### Occurrence of Titanium Minerals in the Saxon Granulites.

By J. LEHMANN (*Jahrb. f. Min.*, 1882, 1, Ref. 411).—The brownish-yellow microscopic prisms in granulite which were regarded by Zirkel as zircon, consist, according to the author, not of zircon but of rutile. He also supposes that the dark capillary enclosures, like gossamer-threads, often found in quartz and less frequently arranged in three bundles intersecting one another at  $60^\circ$ , consist of rutile. When they occur abundantly in quartz in the form of thicker needles, they are often associated with titanite iron. These dark capillary enclosures in quartz were also regarded as rutile by Hawes, on account of their transformation, which he had observed, into unmistakeable rutiles. They are very abundant in the old highly quartziferous rocks (granites and gneisses). Rosenbusch, on the other hand, having failed in the endeavour to isolate them by means of hydrofluoric acid, from the quartz of the Rappakiwi, in which they are very abundant, is not quite convinced of their identity with rutile. H. W.

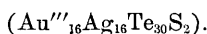
**Mineralogical Observations.** By R. SCHARITZER (*Jahrb. f. Min.*, 1882, 1, Ref. 353).—1. *Occurrence of Microcline, Razamowskin and Beryl in the Neighbourhood of Freistadt in Upper Austria.*—In the coarse-grained granite west of Neumarkt, there occur veins of a fine-grained granite containing portions resembling pegmatite, and in these are found crystals of microcline. The crystals are white to yellowish-white, and when examined with a lens, exhibit two systems of opaque lamellæ intersecting one another at acute angles and imbedded in the transparent mass of felspar. Many of these crystals are Karlsbad twins. Observed faces,  $0P$ ,  $\infty P$ ,  $\infty P\infty$ ,  $P$ ,  $P\infty$ ,  $2P\infty$ ; in one instance the face  $P$  was likewise observed. Angle  $0P : \infty P\infty = 90^\circ 30'$ . Sp. gr. = 2.549. The analysis of the substance, previously ignited with nitric acid, gave 64.040 per cent.  $\text{SiO}_2$ , 18.284  $\text{Al}_2\text{O}_3$ , 0.977  $\text{Fe}_2\text{O}_3$ , 0.927  $\text{CaO}$ , 10.646  $\text{K}_2\text{O}$ , 0.147  $\text{Na}_2\text{O} = 100.021$ . Loss by ignition, 1.366. The ratio of  $R'$  to  $\text{Si}$  in this felspar is 1 : 5.7 instead of 1 : 6. A felspar with such a proportion of alkali should have the composition 10 microcline + 7 albite + 1 anorthite. Its analysis however gives too much alkali, and too little silica and alumina, a difference which cannot be attributed to weathering, as this would produce a change in the contrary direction.

The same pegmatite also contains numerous crystals of beryl, which are opaque to translucent, yellow-brown to red-brown, also green. They exhibit the first and second pyramid, very rarely associated with the basal pinacoid and a pyramid  $3P$ . Angle  $0P : 3P = 119^\circ 30'$ . Those beryls which are imbedded, not in the pegmatite itself, but in

the younger quartz filling its geodes, are all several times fissured in the direction of OP.

**Razumowskin.** In the weathered granite to the south of Freistadt, there occur clefts filled with an apple-green, almost loamy substance, which however soon becomes brittle when taken out; it adheres to the tongue, has a laminar feel and earthy texture, but falls to pieces in water. It is extremely hygroscopic, so that its amount of water varies greatly at different times. An analysis of the substance dried at  $100^{\circ}$  gave 7.436  $\text{H}_2\text{O}$ , 55.080  $\text{SiO}_2$ , 23.375  $\text{Al}_2\text{O}_3$ , 4.415  $\text{Fe}_2\text{O}_3$ , 0.768  $\text{FeO}$ , 1.990  $\text{CaO}$ , 4.004  $\text{MgO}$ , 1.637  $\text{K}_2\text{O}$ , 0.809  $\text{Na}_2\text{O}$ , with traces of  $\text{MnO}$  and  $\text{CO}_2$ . The substance saturated with moisture lost by ignition 17.089 per cent. The author considers that this bole-like substance is most nearly related to the razumowskin of Kosemütz in Silesia.

2. *Gold and Silver Telluride (Krennerite) from Nagjag.*—Sp. gr. = 5.298. Analysis gave 30.032 Au, 16.888 Ag, 39.140 Te, 9.746 Sb (by loss), and 4.394 S = 100. As the mineral probably contained  $\text{Sb}_2\text{S}_3$  mechanically mixed, it may be regarded as consisting of  $\text{Ag}_2\text{Te}$ , having part of the silver replaced by gold ( $\text{Au}'''\text{AgTe}$ ), or in addition, with a small portion of the tellurium replaced by sulphur,



None of the other compounds of gold, silver, and tellurium occurring in nature can be referred to the formula  $\text{Ag}_2\text{Te}$ . Krennerite is therefore a distinct mineral species. H. W.

**Pseudochrysolites (Bottle-stones) of Moravia and Bohemia,** By A. MAROWSKY (*Mineral Mitth.*, 1881, 4, 43—48).—Remarks thereon by G. TSCHERMAK (*ibid.*, 42—50). **The Bottle-stone of Trebitsch.** By F. v. HANER (*Verh. der k. k. geolog. Reichsanstalt*, 1880, 282—224; (*Jahrb. f. Min.*, 1882, 1, Ref., 410).—These formations, formerly regarded as obsidians, have been shown by the experiments of Marowsky and Tschermak to be nothing but artificial products, formed in the manufacture of glass, and thrown away as useless. This view is supported, not only by their occurrence on the gneiss region of Bohemia and Moravia, where no sign of volcanic formations is otherwise visible, and by their want of perfect agreement in fracture, lustre, and colour with true obsidian, but also by their chemical composition, which is somewhat too variable for obsidian from the same locality, and is moreover especially distinguished by the complete absence of potassium, an element which appears to be always present in natural obsidian.

*Analyses* 1 and 2 from Trebitsch; 3 and 4 from Moldauthei.

	$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{MnO}$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{Na}_2\text{O}$ .	Loss by ignition.
(1)	81.21	10.23	2.45	—	2.10	1.08	2.43	0.14 = 99.64
(2)	76.10	5.13	7.13	1.25	4.67	2.95	3.16	— = 100.39
(3)	82.70	9.40	2.35	0.13	1.21	1.21	2.45	— = 99.45
(4)	79.12	11.36	2.38	—	4.45	1.48	1.21	— = 100

Sp. gr. of (1) = 2.35; of (2) = 2.17. H. W.

**Mineralogical Notices.** By E. E. SCHMID (*Jahrb. f. Min.*, 1882, 1, Ref., 352).—1. *Steatargillite*. This name is given to a white or light green mass, greasy to the touch, which fills up the pebbles of certain porphyritic rocks in the neighbourhood of Ilmenau.  $H. = 1.5$ .  $G. = 2.29-2.46$ . Powder attacked by hydrochloric acid. I. Green pebbles from the Höllekopf.  $G. = 3.217$ . II. Green pebbles from the Tragberg.  $G. = 2.465$ . III. White pebbles from the Höllekopf.  $G. = 2.307$ .

	SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	MgO.	FeO.	CaO.	H <sub>2</sub> O.
I.	37.20	25.56	8.09	15.56	3.78	0.98	8.70 = 99.87
II.	32.77	17.73	11.12	14.19	12.51	0.91	9.77 = 99.00
III.	38.67	24.72	10.69	12.95	0.95	1.36	9.65 = 98.99

The variations in the composition of the substance show that it is most probably a mixture.

2. *Datolite* from the Melaphyre of the Schneidemüllerskopf in the Upper Ilmthal. The surface of a cleft in this locality is lined with quartz, on which is implanted, in a layer of crystals, together with calcite and iron pyrites, a colourless mineral, recognised by the author as datolite. An analysis made upon a small quantity gave 39.49 per cent. SiO<sub>2</sub>, 33.81 CaO, 1.03 Fe<sub>2</sub>O<sub>3</sub>, and 5.09 H<sub>2</sub>O. Lime and boric acid were detected qualitatively.

*Pseudo-Gaylussite*. In the dolomite between Amt-Gehren and Königsee, at the foot of the Thüringer Wald, there occur pseudomorphs of calcite after gaylussite in the monoclinic forms  $\infty P$  and  $P$ . Analysis gave 96.5 per cent. CaCO<sub>3</sub>, 0.6 MgCO<sub>3</sub>, 0.9 Na<sub>2</sub>CO<sub>3</sub>, 0.9 H<sub>2</sub>O, and a trace of aluminium silicate.

3. *Scolecite* occurs in the Etzlithal near Amsteg (Reussthal), together with byssolite and stilbite (heulandite), in concentrically radiate groups. The individual needles exhibit the forms  $\infty P$ ,  $P$ ,  $-P$ ; they are colourless, and have a vitreous lustre.  $H. = 5$ .  $G. = 2.27$ . Cleavage distinct parallel to  $\infty P$ . Analysis gave 45.70 per cent. SiO<sub>2</sub>, 27.46 Fe<sub>2</sub>O<sub>3</sub>, 14.29 CaO, 0.06 MgO, 0.11 Na<sub>2</sub>O, 13.45 H<sub>2</sub>O = 101.23.

The admixed *heulandite* exhibits the combination  $\infty P \infty . \infty P \infty . P \infty , 2P$ .

The *byssolite* consists of slender capillary prisms, mixed with dark green six-sided plates and hexagonal prismatic groups of plates, the colour of which nearly resembles that of vermiculite. H. W.

**Pilarite, a New Mineral of the Chrysocolla Group.** By KRAMBERGER (*Zeitschr. f. Kryst.*, 5, 260; *Jahrb. f. Min.*, 1882, 1, Ref., 363).—This mineral, from Chili, has a light greenish-blue colour and somewhat lighter streak. Hardness about 3. Sp. gr. = 2.62. Lustre dull. Disintegrates partially in water. Analysis gave—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CuO.	CaO.	Loss by ignition.
38.6	16.9	19.0	2.5	21.7 = 98.7

leading to the formula  $\text{CaCu}_5\text{Al}_6\text{Si}_{12}\text{O}_{39} + 24\text{Aq}$ . Under the microscope, the mineral appears apolar but nearly homogeneous.

H. W.

**Action of Sulphurous Acid on certain Minerals and Rocks.**

By W. B. SCHMIDT (*Tschermak's Min. Mittheil.*, 1881, **4**, 1—42; *Jahrb. f. Min.*, 1882, **1**, Ref., 408—410).—The experiments recorded in this paper were made with the view of throwing light on the important changes produced in minerals and rocks in certain stages of volcanic activity. Water saturated with sulphurous acid at low temperatures was enclosed in bottles, together with the finely sifted and well-dried powder, and carefully protected from the air. To examine the action of sulphurous acid in the nascent state, experiments were made with hydrogen-sodium sulphite, the solution of which filled about one-fifth of the vessel, the remainder being occupied by air. The bottles remained closed in one case for half a year, in all the others for a year, and were subjected to frequent, and for the most part to daily agitation. The residue and solution were then analysed, and their composition compared with that of the unaltered substance. From the numerical results, which are tabulated in the paper, the author deduces the following general conclusions:—

1. All the minerals and rocks used in the experiments—viz., labradorite, sanidin, quartz, augite, magnesia-mica, basaltic tufa, oligoclase, trachytic conglomerate, and hornblende—were decomposed, some, and in certain cases all their constituents being more or less dissolved.

2. Water saturated with sulphurous acid acted more strongly than the solution of hydrogen-sodium sulphite.

3. The order of solubility of the several constituents is as follows: magnesia, ferric oxide, lime, soda, alumina, potash, silica.

4. The solubility of the several minerals and rocks decreases as the proportion of silica increases; with an equal amount of silica, the proportion of the entire substance dissolved is greater as the other constituents are more soluble and are present in larger proportion.

5. Sulphurous acid acts on the felspars similarly to the constituents of the atmosphere.

6. The quantity of matter dissolved is considerably greater at the beginning of the action than in the subsequent stages.

7. The large proportion of iron dissolved out gives rise to a bleaching of the minerals and rocks.

8. The results of these experiments do not differ essentially from those of the action of acid vapours observed in nature.

9. The sulphuric acid formed in the bottles, in spite of complete filling and air-tight closure, must certainly have had some influence on the results; nevertheless sulphates and sulphites appear to be formed together, both in experiments like those under consideration, and in nature, the sulphites naturally oxidising quickly in contact with the air.

In conclusion, the author discusses the various natural products of formation and transformation, which may be attributed to the action of sulphurous acid, viz., cimolite, pseudomorphs of opal after augite, silicic hydrates, various sulphates, alum-stone, &c. H. W.

**Silurian Rocks in the Territorio d'Iglesias, Sardinia.** By A. COSSA and E. MATTHEOLI (*Atti della R. Accad. delle Scienze, Torino*, vol. **16**, 1881; *Jahrb. f. Min.*, 1882, **1**, Ref., 412).—The clay-slates of this district contain lithium. A nodular mica-slate of Rus in Arrus,

Flumini-Maggiore, agrees exactly in its characters with the mica-slate of Tirpersdorf near Oelsnitz, excepting that it does not contain any green mica. In this slate also lithium was detected by spectroscopic examination. Chemical analysis gave the composition I (*infra*). The argillaceous cement of a sandstone of Acqua Callertis, Flumini-Maggiore, was found to contain fragments of plagioclase crystals, more or less altered.

The eruptive rocks of the district are quartz-porphyrries, *e.g.*, with sphærolithic structure (Santa Lucca, Anal. II), the sphærolites of which consist of radial groups of quartz and felspar, often with an amorphous nucleus, and containing, instead of mica, small quantities of amphibole, mostly chloritised. A microgranitic quartz-porphyr from Genna Arezza, Flumini-Maggiore, gave the composition III; a porphyritic quartz-diorite, the composition IV.

	I.	II.	III.	IV.
Loss by ignition..	3.97	0.69	1.25	3.28
SiO <sub>2</sub> .....	57.83	75.98	69.40	56.13
Al <sub>2</sub> O <sub>3</sub> .....	20.55	14.76	17.73	15.93
Fe <sub>2</sub> O <sub>3</sub> .....	8.73	—	0.51	8.60
CaO .....	trace	—	trace	4.99
MgO .....	3.39	—	—	5.12
K <sub>2</sub> O .....	3.32	4.12	7.39	5.95
Na <sub>2</sub> O .....	0.92	3.65	3.00	
	98.71	99.20	99.28	100.00
Sp. gr.....	2.78 (10°C.); 2.61 (9.5°); 2.54 (9°); 2.75 (9°).			
	H. W.			

**Notes on the Diabase Rocks of the Buchan District.** By A. W. HEWITT (Roy. Soc. of Victoria, Melbourne, 1881; *Jahrb. f. Min.*, 1882, 1, Ref., 414).—In the district between the Buchan and Snowy rivers, North Gippsland, Victoria, there occur Middle Devonian strata, the age of which may be precisely determined, by their characteristic fauna, as belonging to the Buchan limestones. On the slope of these limestones are found beds of a basic eruptive rock, partly of compact structure, partly blistered even on the surface, in connection with tuffaceous and breccia-like layers. A very careful microscopical and chemical examination of these eruptive masses demonstrated the existence, in those from the valley of the Snowy River, near Moore's Crossing, of a typical enstatiferous diabase-porphyr, with a nearly holocrystalline ground-mass consisting chiefly of splinters of plagioclase.

The structure and transformation-phenomena of the components of this rock are similar to those of analogous European formations. Chemical treatment of thin sections showed that the plagioclase splinters of the ground-mass resist the action of hydrochloric acid much more strongly than the disseminated crystals of the same mineral, whence it may be inferred that they are more acid. An analysis of this enstatiferous diabase-porphyr is given under I.

Further west, in the neighbourhood of the Murendel Mine, there occur basic eruptive rocks, forming veins in the lower Buchan strata;

the same rocks occur also frequently under similar relations on the line between the Snowy and Murendel rivers. Black, dense, and fresh in aspect, they present the characters of nearly holocrystalline diabase-porphyrates with smaller interspersed crystals of plagioclase, augite, and magnetite, together with microscopic needles of quartz, calcite, and delossite; identical therefore in all essential particulars with the diabase-porphyrates on the slope of the upper Buchan layers in the Snowy River valley.

On the slope of the Devonian limestone at the confluence of the Buchan and Murendel rivers, there occur fine-grained holocrystalline diabbases of normal structure containing splinters of plagioclase, which form a regular network, having its meshes filled up with augite. Separate plagioclase crystals, and somewhat more numerous augite-crystals, occur in them porphyritically, producing an approximation to the porphyritic structure. Quantitative analysis gave the values II. The rock is evidently not so felspathic as the diabase porphyries.

West of the Murendel river are found oliviniferous plagioclase-augitic rocks, through which is bored the entrance to the Murendel South Mine. The author is inclined to regard these rocks also as Devonian, and to place them with the melaphyres, but refers to future communications for the more complete establishment of this view.

	I.	II.		I.	II.
SiO <sub>2</sub> .....	53.39	48.48	H <sub>2</sub> O .....	1.14	1.72
Al <sub>2</sub> O <sub>3</sub> .....	15.23	14.57	CO <sub>2</sub> .....	0.22	1.27
Fe <sub>2</sub> O <sub>3</sub> .....	8.73	11.68	P <sub>2</sub> O <sub>5</sub> .....	0.16	0.45
FeO.....	3.61	2.83		100.50	101.21
CaO.....	8.46	9.56			
MgO .....	4.12	5.55	Hygr. water..	0.60	0.85
K <sub>2</sub> O.....	1.84	1.77	Pyrites .....	0.16	—
Na <sub>2</sub> O .....	3.60	3.33	Sp. gr. ....	2.814	2.807

H. W.

**Mineralogical Composition of the Normal Mesozoic Diabase on the Atlantic Border.** By G. W. HAWES (*Proc. U. S. National Museum*, 1881, 129, 134; *Jahrb. f. Min.*, 1882, I, Ref., 414).—From a diabase forming veins in the triassic sandstone of the east coast of the United States (locality, Jersey City), the felspathic constituent could be separated by the use of a solution of potassio-mercuric iodide into two portions, one of which, of sp. gr. > 6.9, gave by analysis the composition I; the other of sp. gr. < 6.9, the composition II.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.
I.	52.84	28.62	1.52	11.81	0.46	2.38	0.86	1.06 = 99.55
II.	60.54	24.11	1.14	9.15	0.27	4.11	1.06	0.59 = 100.97

These analyses show that the heavier felspar consists of labradorite, the lighter of andesite. The powders of the two could be distinguished microscopically. It is worthy of note that these typically granular diabbases have in many places borders rich in glass, and exhibiting the structure of augite-andesites.

H. W.



**Serpentine-rocks of the St. Gothard, of the Bobbiese Apennine, and of Monteferrato, near Prato.** By A. COSSA (*Jahrb. f. Min.*, 1882, 1, Ref., 418—420).—The serpentines of the St. Gothard have been supposed by Sjögren to originate from pyroxene rocks, by Staff and Fischer from olivin rocks (*Jahrbuch*, 1882, 1, Ref., 46 and 67).

Cossa finds that both these statements are correct, but that they probably relate to serpentine from different parts of the mountain. Specimens of rock taken from the tunnel at 4870·8 and 5250 meters from the north end were found by analysis to consist, not of serpentine, but of mixtures of talc, a monoclinic pyroxene not containing diallage, and olivin in varying proportions, the former exhibiting but slight, the latter very abundant indications of commencing serpentinisation. On the other hand, two specimens taken at 5250 and 5306·2 meters from the north end of the tunnel exhibited the composition of true olivin-serpentines, like those of Corio, Verrayes, and Favaro, with scanty residues of pyroxene and talc.

The serpentine from the Apennine of Bobbio (from the valley between Sta. Margherita and Prella, south of Varro, and from the neighbourhood of the Rovegno copper mine, south of Ottone) are partly enstatite-serpentines, like that from the first-mentioned locality, having a porphyritic structure due to disseminated bastite, partly pure olivin-serpentines, like that last mentioned. The bastite of the former locality was found to contain 14·65 per cent.  $H_2O$ , 38·22  $SiO_2$ , 14·05  $FeO$  with traces of  $Cr_2O_3$ , 32·83  $MgO$ , and traces of lime and alumina. From the olivin-serpentine of Rovegno, yellow-brown transparent picotite may be easily separated by hydrochloric acid.

Of the celebrated serpentines and gabbros in the neighbourhood of Prato, near Florence, the following were examined:—1. *Serpentine* from the Benini quarry, Monteferrato, formed from a mixture of olivin and a pyroxenic mineral, which probably was originally diallage, but has been converted into a mineral resembling bastite (Anal. I). 2. *Spotted Serpentine* from Montemezzano, near Prato, very much like that of Impruneta, and originating from a rhombic mineral. The lighter spots are produced by the local absence of an ore-constituent, composed for the most part of chromite (Anal. II). 3. *Serpentine* (*Verde di Prato*) from the Benini quarry, originating from a mixture of olivin and a rhombic mineral having the structure of bastite, which mineral appears to have been formed from diallage, but no longer contains lime (Anal. III). The ore (magnetite) is essentially concentrated in the lamellar mineral, and only sparingly present in the serpentine. 4. Gabbro from the quarries of Acqua del Prato. 5. Diabase from Monteferrato, near Prato. According to Giordano, it forms blocks and concretionary masses in the gabbro near the serpentine which overlies it. It has a dark blue-black colour; is homogeneous and very dense; has a splintery fracture, the true structure and composition of diabase, and a very fine grain. The narrow felspar-splinters are in some parts strongly kaolinised, in others transformed into a mass of confusedly interlaced crystals, "like those which are seen in the contact-rocks of diabase and gabbro, and gradually pass into variolites." The augite which cements together the splinters of

plagioclase is partly converted into a substance resembling bastite (Anal. IV). 6. In the clefts of the serpentine of Monteferrato, there is found, though rarely, a silver-white to light-greenish talc-like substance, having a laminar structure, optically biaxial, very difficultly fusible in thin laminae; it has the composition of chlorite (Anal. VI).

	I.	II.	III.	IV.	V.	VI.
Loss by ignition	13.23	12.10	13.90	1.27	3.95	—
SiO <sub>2</sub> .....	38.70	39.77	38.94	51.09	48.20	31.79
Al <sub>2</sub> O <sub>3</sub> .....	0.58	trace	—	8.24	16.48	16.89
Fe <sub>2</sub> O <sub>3</sub> .....	3.19	1.76	1.18	—	7.56	—
Cr <sub>2</sub> O <sub>3</sub> .....	0.39	0.36	0.29	trace	trace	trace
FeO .....	7.26	8.48	8.25 <sup>(1)</sup>	6.91	1.04	6.28 <sup>(1)</sup>
CaO .....	trace	trace	trace	12.75	7.87	trace
MgO .....	36.44	37.33	37.28	19.38	8.93	32.38
Na <sub>2</sub> O .....	—	—	—	—	4.41	—
K <sub>2</sub> O .....	—	—	—	—	0.56	—
H <sub>2</sub> O .....	—	—	—	—	—	12.72
	99.79	99.80	99.84	99.64	99.07 <sup>(3)</sup>	100.06
Sp. gr. ....	2.55	2.56	2.57	2.37 <sup>(2)</sup>	2.85	
at	13°	13°	6°	12° C.		

H. W.

<sup>(1)</sup> With traces of NiO.<sup>(2)</sup> Probably a misprint.<sup>(3)</sup> Together with 0.29 TiO<sub>2</sub> and 0.34 P<sub>2</sub>O<sub>5</sub>.<sup>(4)</sup> With traces of MnO.

**Picrite-porphry of Steierdorf in the Bannat.** By E. HUSSAK (*Jahrb. f. Min.*, 1882, **1**, Ref., 420).—This eruptive rock, described by Kudernatsch as felsite-porphry, forms a layer between the coal and bituminous lias-shale in the Anina shaft at Steierdorf, where it has converted the adjacent coal into coke, and has likewise altered the amount and composition of the bituminous substances in the lias-shale. Small cavities of the rock, at most 1 mm. in diameter, contain a partly yellow, partly brown, waxy substance, which burns readily, emitting an aromatic odour, may be extracted by ether from the pulverised rock to the amount of  $\frac{1}{2}$  per cent., and is nearly related to ozokerite. Moreover, there exudes from geodes lined with rhombohedrons of calcite, a watery liquid having a faint odour of petroleum. These hydrocarbons are probably derived from the neighbouring rocks. The eruptive rock itself is black, has the aspect of melaphyre, and contains disseminated crystals of olivin having a grey crust arising from decomposition, and granules of quartz. Microscopic investigation shows, as chief constituents, olivin, augite, and hornblende all well crystallised. Calcite appears as a product of decomposition. The author regards the rock as closely allied to the picrite-porphyrries of Moravia. H. W.

**Phonolite.** By K. F. FÖHR (*Jahrb. f. Min.*, 1882, **1**, Ref., 413).—The author finds that all phonolites contain fluorine, which apparently does not belong to the apatite contained in them. Some contain copper and antimony; those of Marienberg near Aussig, also those of

the Brüxer, Schlossberg, and Hohentwiel, and the leucite porphyry of Olbrück, contain zinc and lead; in those of the Brüxer Schlossberg and of Olbersdorf, near Zittau, chromic oxide was detected, and more widely distributed, zirconia. The heavy metals are found in that portion of the phonolites which is undecomposable by hydrochloric acid. Cerite metals were not detected. H. W.

**Investigations of the Greenstones. Melaphyre.** By T. PETERSEN (*J. pr. Chem.* [2], 23, 402—411).—This is an account of an examination of specimens of melaphyre, taken from a vein in the Gran Mulatto, N.E. of Predazzo, in the Fassathal.

1. *Porphyritic Melaphyre*.—The ground-mass of this stone is a dark bluish-grey; it contains particles of magnetic oxide of iron, felspar, augite, olivine, small quantities of titanite iron ore, and probably apatite. The stone has a splintery uneven fracture; in powder it is a greenish-grey, becoming light brown after ignition. Sp. gr. 2.793 at 17°.

2. *Dioritic Melaphyre*.—The sp. gr. of this more compact melaphyre is 2.904 at 17°; in a state of powder it is greenish-grey; in massive state it is blackish-grey.

The following table contains the results of the analysis of the above:—

	Soluble in Hydrochloric Acid.		Insoluble in Hydrochloric Acid.		Total.	
	I.	II.	I.	II.	I.	II.
Silica .....	17.64	18.27	37.38	33.14	55.02	51.41
Titanic oxide....	0.40	0.64	—	—	0.40	0.64
Alumina .....	12.07	12.31	9.65	7.05	21.72	19.36
Ferric oxide ....	2.29	4.28	—	—	2.29	4.28
Ferrous oxide ..	3.29	5.35	1.24	1.28	4.53	6.64
Lime .....	4.30	4.75	2.47	2.68	6.77	7.43
Magnesia .....	1.14	1.78	0.69	1.08	1.83	2.86
Soda .....	0.51	1.11	2.21	1.59	2.72	2.70
Potash .....	0.66	0.89	2.75	0.92	3.41	1.81
Water .....	0.40	0.39	—	—	0.40	0.39
Phosphoric acid .	0.37	0.42	—	—	0.37	0.42
	43.07	50.19	56.39	47.74	99.46	97.93

Traces of manganese, copper, barium, carbonates, chlorides, and sulphides were also found in each.

The author also gives the following analysis of plagioclase crystals separated from the melaphyre, which contains hornblende crystals, and is found on the south of the Monto Mulatto. These plagioclase crystals have been studied by v. Rath, who regarded them as andesin (*Pogg. Ann.*, 144, 242). The author finds that acetic acid extracts calcium carbonate and apatite from apparently pure crystals, and hence the calcium will be a little too high. The author finds more silica than given by v. Rath, and is inclined to regard these crystals as belonging to the oligoclase class. The sp. gr. is 2.674.

Silica.	Alumina.	Lime.	Magnesia.	Soda.	Potash.	Water and Carbon Dioxide.
62.84	23.53	5.50	trace	7.65	1.15	traces
P. P. B.						

**Analysis of the Deposit from the Waters of Schinznach.**  
By OBERLIN and SCHLAGDENHAUFFEN (*J. Pharm. Chim.* [5], 5, 360—364).—The deposit from these waters occurs as brittle plates, having the colour of crude sulphur, mixed with fragments of dark coloured wood. According to Banhof it consists chiefly of magnesium and calcium carbonate, together with small quantities of calcium sulphate and sulphur.

The authors' results differ materially from Banhof's, since they prove the presence of free sulphuric acid, and this makes the presence of carbonates impossible; the deposit, therefore, is not identical with that examined by Banhof. After extraction with carbon bisulphide, the residue gave the following results:—

CaSO <sub>4</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	SO <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .
5.4433	0.2250	0.0170	0.0009	0.0545	3.9844	0.4500 = 10.1751

On treating the deposit with boiling water, the solution gave the following results:—

CaSO <sub>4</sub> .	FeSO <sub>4</sub> .	MgSO <sub>4</sub> .	K <sub>2</sub> SO <sub>4</sub> .	Na <sub>2</sub> SO <sub>4</sub> .	SO <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .
1.4515	0.2110	0.0135	0.0013	0.0333	1.0625	0.1200 = 2.8931

0.12 ferric oxide per 100 parts of total residue was extracted by nitric acid from the residue left after treatment with hot water.

Besides the above substances, the authors detected the presence of arsenic in these deposits.

L. T. O'S.

## Organic Chemistry.

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**Action of Potassium Sulphide on Chloroform.** By W. W. J. NICOL (*Proc. Roy. Soc. Edin.*, **10**, 425).—Unlike the compound prepared by Pfannkuch (this Journal, 1873, 363), the action of potassium sulphide on chloroform is to produce potassium sulphydrate and potassium thioformate (KHCOS), which is converted into the formate by mercuric oxide. The free acid could not be prepared.

E. W. P.

**Trichloropropane;  $\beta$ -Chloropropylidene Chloride.** By P. v. ROMBURGH (*Bull. Soc. Chim.* [2], **37**, 98—103).—That portion of the product of the action of phosphorus pentachloride on acrolein (this vol., p. 376) which boiled above 120° was fractionated, and the fractions passing over between 120° and 140°, and 140° and 150°, were treated with chlorine and again fractionated. In this way a

*trichloropropane*,  $C_3H_5Cl_3$ , is obtained; b. p.  $146-148^\circ$ ; sp. gr. at  $15^\circ = 1.362$ ; vapour-density, 4.95. It exerts no action on polarised light. Heated with potash, it is attacked with some difficulty, yielding allylidene chloride, b. p.  $85^\circ$ , and a small quantity of  $\beta$ -chlorallyl chloride. It is therefore  $CHCl_2.CH_2.CH_2Cl$ , or  $\beta$ -chloropropylidene chloride, the hitherto unknown isomeride of trichlorhydrin.

Geuther has stated that acrolein hydrochloride, when heated with phosphorus pentachloride, yields ordinary trichlorhydrin, but the author finds that this reaction yields the  $\beta$ -chloropropylidene chloride previously described, thus confirming Krestownikoff's supposition that acrolein hydrochloride is  $\beta$ -chloropropionic aldehyde. C. H. B.

**Normal Cyanic Acid,  $N:C.OH$ , and its Derivatives.** By E. MULDER (*Ber.*, 15, 69—71).—The author's results as regards the metallic salts of this acid confirm those of Bannow (*ibid.*, 4, 254; 13, 226). By the action of cyanogen on sodium cyanimide, a dark coloured mass is obtained, whilst cyanogen does not react with cyanamide itself. A body,  $N:C.OEt$ , crystallising in prisms (m. p.  $29^\circ$ ) and decomposed by potash with formation of cyanuric acid, is obtained along with some liquid product, when cyanogen bromide is added to sodium ethylate, both in ethereal solution. D. A. L.

**Symmetrical Dichlorethyl Oxide.** By HANRIOT (*Ann. Chim. Phys.* [5], 25, 219—225).—Aldehyde reacts with acetic chloride and acetic anhydride to form compounds which may be considered to be ethereal salts of ethylidene glycol; but this latter substance has never been isolated, for both the glycol itself and its derivatives readily give up a molecule of water, with formation of aldehyde derivatives.

By passing a slow current of dry hydrochloric acid through well cooled aldehyde, and distilling the product immediately in a vacuum, a liquid is obtained (b. p.  $25-30^\circ$ , at pressure of 1 cm. mercury) of the composition  $CHMe(OH)Cl$ , and is the mono-chlorhydrin of ethylidene glycol. It is quickly decomposed into water and symmetrical dichlorethyl oxide,  $2CHMe(OH)Cl - OH_2 = CHMeCl.O.CHMeCl$ . But this reaction is best effected by saturating aldehyde with excess of hydrochloric acid, when besides dichlorethyl oxide other condensation products are formed. Dichlorethyl oxide is a heavy liquid (b. p.  $52^\circ$  under 4 cm. of mercury); it is very stable when pure, but is rapidly decomposed if contaminated with but small quantities of water and hydrochloric acid. It is not attacked by boiling water, but is attacked readily by potash. Its constitution was ascertained from its reactions with zinc-ethyl, sodium ethylate, and ammonia. Zinc-ethyl forms a secondary butyl oxide,  $CHMeEt.O.CHMeEt$  (b. p.  $123^\circ$ ); sodium ethylate replaces one of the chlorine-atoms by the grouping ethoxide, producing a compound of formula  $CHMeCl.O.CHMe.OEt$ , a colourless, stable liquid (b. p.  $146^\circ$ ); ammonia replaces both the chlorine-atoms, to give the hydrochloride of an anhydride of aldehyde-ammonia,  $CHMe(NH_2)O.CHMe(NH_2), 2HCl$ . This substance forms colourless crystals, which effloresce rapidly in the air, and give off hydrochloric acid; aniline and toluidine form analogous compounds.

V. H. V.

**Gum Arabic.** By H. KILIANI (*Ber.*, **15**, 34—37).—This is a reply to Claësson (*Abstr.*, 1881, 795—796), who disputed the facts of a previous paper by the author (*ibid.*, 243), stating that arabinose is not identical with lactose, and that only those specimens of gum arabic which yield very little or no mucic acid on oxidation with nitric acid, contain arabinose. The author has examined several specimens of gum arabic, including one from Claësson containing arabinose. The mucic acid is estimated in the following manner:—1·5—2 grams of powdered gum are digested at 60° with three times the weight of nitric acid, sp. gr. 1·2, until the whole becomes one solid mass saturated with the liquid. To this is added a like quantity of nitric acid, and it is then brought on to a weighed filter. The residue on the filter is washed thoroughly, and then dried at 100° and weighed. The filtrate and washings are mixed, evaporated down, oxidised with nitric acid, &c., as above. A third oxidation generally yields only a trace of mucic acid. The results of the analyses, &c., are tabulated in the annexed table:—

Name.	Description.	Mucic acid per cent. in air-dried gum.	Rotation.
1. East Indian gum	Mostly topaz-coloured pieces, some yellow, with pores, a very few colourless long pieces; only a few large lumps	14·3	Right
2. Mogadore gum	Chiefly yellow and red middle-sized pieces mixed with smaller and colourless; contained a quantity of impurities, dust, &c.	14·6	„
3. Claësson's gum	Small pieces, partly colourless, partly yellow	19·5	„
4. Gum arabic, Suakin	Unequal, colourless, yellow, and deep red coloured pieces, some long, pale yellow, and partly opaque	21·5	„
5. Gum arabic, elect. I	Almost colourless, mostly small angular pieces, evidently fragments of the large round lumps full of cracks, which are present	20·7	„
6. Gum Senegal, bas du fleuve	Very large bright-yellow transparent lumps, with large air-bubbles and nodular projections on the surface	21·0	Left
7. Arabic acid . . .	Prepared from lævo-rotatory gum by Neubauer's method, and from which the author first obtained lactose	a. 23·9 b. 24·4	„ „
8. Gum arabic, elect. 0	Externally like 5 . . . . .	23·9	„
9. Gum arabic, nat. III, best natural Cordofan gum	Lumps larger than 5, very equal in size, yellowish, opaque, full of cracks	24·0	„
10. Australian gum	Large red-brown hemispherical pieces, or stalactites with a flat side	38·3	„

The above method is frequently employed to determine if the sugar from gum contains lactose, and in what quantity. Lactose both from milk-sugar and from gum yields in one oxidation between 60—70 per cent. mucic acid. The method is also useful for the quantitative investigation of the changes which gums undergo by treatment with dilute sulphuric acid. The author has observed a small quantity of a sugar other than lactose, in Claësson's gum. If this is the arabinose, he cannot understand how Scheibler has obtained it without lactose. He tried an experiment with dilute sulphuric acid and gum at 100°, and even then obtained lactose.

D. A. L.

**Note on a Crystalline Compound formed in Water containing Hydrogen Sulphide and Mercaptan.** By J. A. BLAICKIE (*Proc. Roy. Soc. Edin.*, 10, 87—89).—During the preparation of mercaptan from ethyl sulphate and potassium sulphhydrate, crystals were formed in the receiver; these crystals were also formed when mercaptan was poured into sulphuretted hydrogen water at 0°; also when sulphuretted hydrogen was passed into water saturated with mercaptan, crystallisation occurred in a few minutes, and a large amount of sulphuretted hydrogen was absorbed. These crystals, which seem to consist of 90 per cent. water, with mercaptan and sulphuretted hydrogen, melt in the mother-liquor above 3°, but at 0° when dried; their specific gravity is above that of the mother-liquor and of ice, and they are soluble in alcohol at -10°, with evolution of a little sulphuretted hydrogen.

E. W. P.

**Method of Preparing Methylamine.** By R. M. MORRISON (*Proc. Roy. Soc. Edin.*, 10, 275).—Dry methylammonium sulphate is heated in sealed tubes at 300°, when the whole is converted into methylamine sulphate. The salt so formed is distilled with potash, and the gas evolved is collected in hydrochloric acid, from which it may be separated by lime.

E. W. P.

**Action of Heat on the Salts of Trimethylsulphine.** By A. CRUM BROWN and J. A. BLAICKIE (*Proc. Roy. Soc. Edin.*, 10, 53—55; and 253).—The acetate, which will not crystallise when heated, is decomposed into water, methyl sulphide, and methyl acetate; the last two distil over together at 45—50°, and cannot be separated by distillation, but a separation may be effected by means of mercury chloride.

At 110° the thick aqueous solution of the benzoate yields methyl sulphide and methyl benzoate. The dithionate at 120° loses its molecule of crystalline water, and at 220° sulphurous anhydride is given off; continued heating at this temperature removes methyl sulphide, methylsulphate of trimethylsulphine,  $\text{MeSO}_4 \cdot \text{Me}_3\text{S}$  remaining.

The carbonate crystallising in hygroscopic alkaline prisms at 100°, yields water, methyl sulphide, and carbonic anhydride. Heated in sealed tubes at 100°, carbonic anhydride is produced, together with methyl sulphide, water, and methyl alcohol.

The metaphosphate, which does not crystallise, gives off methyl sulphide, and the resulting product is at the same time decomposed,

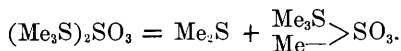


leaving free metaphosphoric acid. Trimethylsulphine ferrocyanide appears as pale green transparent plates, which over sulphuric acid lose 18 mols.  $\text{H}_2\text{O}$ . At  $220^\circ$  hydrocyanic acid, methyl sulphide, &c., are given off. The ferriocyanide acts similarly to the ferrocyanide, and loses 15 mols.  $\text{H}_2\text{O}$ . E. W. P.

**Trimethylsulphine Salts.** By A. CRUM BROWN and J. A. BLAICKIE (*J. pr. Chem.* [2], **23**, 395–401).—*Trimethylsulphine thio-sulphate*  $(\text{Me}_3\text{S})_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}$ , is formed in the oxidation of trimethylsulphine sulphhydrate by exposure to the air. It is a deliquescent salt, crystallising from alcohol in long, transparent quadratic prisms. Exposed over phosphorus pentoxide it loses 1 mol.  $\text{H}_2\text{O}$ , and when heated to  $135^\circ$  it is resolved into methyl sulphide and trimethylsulphine methyl thiosulphate, thus:—

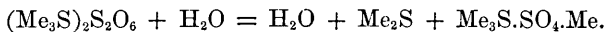


*Trimethylsulphine sulphite*  $(\text{Me}_3\text{S})_2\text{SO}_3$ , is obtained by adding to a portion of methylsulphine hydroxide saturated with sulphurous anhydride an equal amount of the sulphine hydroxide. It is a crystalline salt, and has an alkaline reaction; potassium iodide converts it into trimethylsulphine iodide and potassium methyl sulphate. It is resolved by heat into methyl sulphide and trimethylsulphine methyl sulphonate, thus:—



*Trimethylsulphine oxalate*  $(\text{Me}_3\text{S})_2\text{C}_2\text{O}_4 + \text{H}_2\text{O}$ , is obtained by the action of silver oxalate on trimethylsulphine iodide; it forms large deliquescent tablets, containing 1 mol.  $\text{H}_2\text{O}$ . Heated to  $110^\circ$ , it loses the water of crystallisation, and at  $146^\circ$  is resolved into methyl sulphide and methyl oxalate.

*Trimethylsulphine dithionate*  $(\text{Me}_3\text{S})_2\text{S}_2\text{O}_6 + \text{H}_2\text{O}$ , is obtained by neutralising dithionic acid with trimethylsulphine hydroxide; it forms cube-like crystals, non-deliquescent, and insoluble in alcohol. At  $120^\circ$ , it loses water, and at  $220^\circ$ , it is resolved into sulphurous anhydride, methyl sulphide, and trimethylsulphine methyl sulphate and water, thus:—



The authors have also prepared the acetate, benzoate, and carbonate by the action of trimethylsulphine iodide on the corresponding silver salts.

These salts are extremely soluble in water. A solution of trimethylsulphine sulphide has been obtained by saturating a solution of trimethylsulphine hydroxide with hydrogen sulphide, and then adding to this an equal amount of the hydroxide. On concentration, even in the cold, this solution decomposes into methyl sulphide.

P. P. B.

**Constitution of Guaiac.** By J. HERZIG (*Monatsh. Chem.*, **3**, 118–125).—This compound (commonly called guaiol) is one of the products of the dry distillation of guaiacum (p. 212 of this volume).

It is never obtained quite colourless, but always leaves on distillation a small quantity of brown residue having a higher boiling point. When freed, as far as possible, from this substance, it boils at 118—121°. Contrary to the statement of some chemists who have worked upon it, guaial forms with a strong solution of hydrogen-sodium sulphite (sp. gr. 1.3), a crystalline compound from which it cannot be recovered by the action of sodium carbonate, resembling in this respect the unsaturated aldehydes, acrolein and crotonic aldehyde. It further exhibits the character of an aldehyde in reducing silver-salts, and in oxidising when exposed to the air or treated with mercuric oxide, being thereby converted into tiglic or methylcrotonic acid. Hence guaial consists of tiglic aldehyde,  $\text{CH}_3\text{CH}:\text{CMe.COH}$  (Gerhardt regarded it as the isomeric compound angelic aldehyde), and is identical with that which Lieben and Zeisel obtained (1881, Abstr., 710) as a condensation-product of acetic and propionic aldehydes:  $\text{C}_2\text{H}_4\text{O} + \text{C}_3\text{H}_6\text{O} - \text{H}_2\text{O} = \text{C}_5\text{H}_8\text{O}$ .

By reduction with iron and acetic acid, it yields, like other aldehydes of the same series: (1.) A saturated aldehyde, viz., valeral,  $\text{C}_5\text{H}_{10}\text{O}$  (b. p. 90—92°). (2.) A mixture of a saturated and an unsaturated alcohol (boiling at 125—126°), and a saturated alcohol, viz., amyl alcohol, boiling at 125—126°. (3.) A pentenyl alcohol,  $\text{C}_5\text{H}_9(\text{OH})$ . The same products were obtained by Lieben and Zeisel from their synthetically formed tiglic aldehyde.

Amongst the constituents of guaiacum, there are only three, viz., guaiaretic, guaiacylic and guaiaconic acids, which can be regarded as sources of guaial. The first of these, however, yields by dry distillation only guaicol and pyroguaiacin, no guaial; the second, on the other hand, is completely resolved according to Deville (*Compt. rend.*, 19, 137) into carbonic anhydride and guaial; but the amount of guaiacylic acid contained in the resin is much too small to account for the quantity of guaial resulting from its dry distillation. It seems, therefore, most probable that the chief source of the guaial is the guaiaconic acid, in which it exists ready formed. In fact, when this acid is heated at 170—180° in a sealed tube with hydrochloric acid saturated at 0°, methyl chloride escapes on opening the tube, and the contents yield to ether a body which, from its iron-reaction, its melting point, and other properties, appears to be catechol. H. W.

**Note on Popoff's Law of the Oxidation of Ketones.** By E. WAGNER (*Jour. Russ. Chem. Soc.*, 1882, 113).—According to one of Popoff's laws, "On oxidising ketones in which both carbon-atoms in the neighbourhood of the carbonyl-group contain the same quantity of hydrogen-atoms, i.e., in which the radicals are of the same (or a slightly different) constitution, but not equally large, that carbon-atom is oxidised which belongs to the larger alcohol-radical, the carbonyl-group remaining always with the smaller alcohol-radical."

This thesis has been deduced from one experiment only, made by Popoff himself, and later on confirmed by Völker (*Sitzungsber. Wiener Akademie*, 73 [2], 335; note by the Abstractor), who on oxidising ethyl-propyl ketone, obtained propionic acid.

This is contradicted by the author's experiments, who on oxidising

the latter ketone obtained butyric and acetic acids, and no propionic acid.

In the same manner ethyl-isobutyl ketone yields isovaleric and acetic acids. In these two cases the carbonyl remains with the larger alcohol-radical, in contradiction to Popoff's law. The author is now investigating the oxidation of ethyl-hexyl (norm.), propyl-isobutyl, and propyl-hexyl (norm.) ketones. B. B.

**Researches on the Determination of the Chemical Value of the Constituents of Organic Acids.** By N. MENSCHUTKIN (*Jour. Russ. Chem. Soc.*, 1882, 114—124).—In two former papers the author explained the methods of determining the reaction value of organic bodies, especially of alcohols in the formation of ethereal salts.

The object of the present investigation is to determine the reaction value of organic acids. The monobasic organic acids  $R\cdot COOH$  are made up of two components: the *constant*  $COOH$  and the *variable*  $R$ . The author starts from formic acid,  $H\cdot COOH$ , in which the  $H$ -atom may be replaced by primary, secondary, or tertiary alcohol-radicals.

The values of etherification of this acid are taken as a standard for comparison, the velocity as well as the limit of etherification being = 100. By taking the etherification values of the other acids, and comparing them with that of formic acid, the chemical value of the different variable constituents of the acids may be measured by the number of molecules of the ethereal salts formed.

(1.) *Primary Monobasic Acids.*—The constant constituent of the acids represents the capability of the acids for combination. The numerical values refer to the above-mentioned standard of etherification. The following numbers may serve as an example of the values in the isobutylic system:—

Series.	Coefficients of combination.	
	Velocity.	Limit.
$C_nH_{2n}O_2$ : Formic acid, $CH_2O_2$ .....	100·0	100·0
Acetic „ $C_2H_4O_2$ .....	71·9	104·8
Propionic acid, $C_3H_6O_2$ .....	66·7	106·9
N. butyric „ $C_4H_8O_2$ .....	53·9	108·2
N. caproic „ $C_6H_{12}O_2$ .....	53·6	108·7
N. caprylic acid, $C_8H_{16}O_2$ .....	50·0	110·3
$C_nH_{2n-2}O_2$ Hydrosorbic „ $C_6H_{10}O_2$ .....	69·7	110·4
$C_nH_{2n-8}O_2$ Phenylacetic „ $C_8H_8O_2$ .....	79·1	115·0
Phenylpropionic acid, $C_9H_{10}O_2$ ..	65·2	112·1

Very nearly the same values are obtained in the ethylic system, so that the nature of the alcohol does not seem to have any influence. The velocities of the saturated acids are larger than those of the corresponding unsaturated acids.

In order to find the chemical value of the constant constituents of primary monobasic acids, the above formulæ and numbers are compared with those of formic acid. The numbers below give the difference of the number of molecules of ethereal salts formed, viz.:—

Primary residues.	Values of reaction.	
	Velocity.	Limit.
$\text{CH}_3$ .....	— 28·1	+ 4·8
$\text{CH}_3\text{CH}_2 \dots = \text{C}_2\text{H}_5$ .....	— 33·3	+ 6·9
$\text{CH}_3(\text{CH}_2)_2 \dots = \text{C}_3\text{H}_7$ .....	— 46·1	+ 8·2
$\text{CH}_3(\text{CH}_2)_3 \dots = \text{C}_4\text{H}_9$ .....	— 46·4	+ 8·7
$\text{CH}_3(\text{CH}_2)_4 \dots = \text{C}_5\text{H}_{11}$ .....	— 50·0	+ 10·3
$\text{C}_4\text{H}_7\text{CH}_2 \dots = \text{C}_5\text{H}_9$ .....	— 30·3	+ 10·4
$\text{C}_6\text{H}_5\text{CH}_2 \dots = \text{C}_7\text{H}_7$ .....	— 20·9	+ 15·0
$\text{C}_6\text{H}_5(\text{CH}_2)_2 = \text{C}_8\text{H}_9$ .....	— 34·8	+ 12·1

Compared with formic acid, all the primary acids show smaller velocities and larger limits of etherification. The less saturated the residues are and the more carbon-atoms they contain, the larger are the differences. In the acids with an increasing number of hydrogen-atoms, the acid properties diminish, because the limit of etherification becomes lower, whereas the reverse is the case if the H-atom of formic acid is replaced by hydrocarbon-residues. This is due to the metallic nature of hydrogen; as in the case of alcohols, the values of etherification increase if the variable constituent is hydrogen.

(II.) *Secondary Monobasic Acids.*

Series.	Coefficient of combination.	
	Velocity.	Limit.
$\text{C}_n\text{H}_{2n}\text{O}_2$ .. Dimethyl-oxalic acid, $\text{C}_4\text{H}_6\text{O}_2$ ....	43·4	108·2
Methyl-ethyl oxalic acid, $\text{C}_5\text{H}_{10}\text{O}_2$	30·3	114·8
$\text{C}_n\text{H}_{2n-2}\text{O}_2$ Crotonic acid, $\text{C}_4\text{H}_6\text{O}_2$ .....	19·6	112·3
$\text{C}_n\text{H}_{2n-10}\text{O}_2$ Cinnamic ,, $\text{C}_9\text{H}_8\text{O}_2$ .....	18·7	116·3

The coefficient of velocity of the above acids alone differs from those of primary acids, being considerably smaller (*e.g.*, comparing isobutyric acid (43·4) with normal butyric acid (53·9). The values of reaction of the secondary hydrocarbon residues RCH are:—

Secondary residues.	Values of reaction.	
	Velocity.	Limit.
$\text{Me}_2\text{CH} = \text{C}_4\text{H}_7$ .....	— 53·0	+ 8·2
$\text{Me.Et.CH} = \text{C}_4\text{H}_9$ .....	— 64·4	+ 14·8
$\text{Me.CH.CH} = \text{C}_3\text{H}_5$ .....	— 80·4	+ 12·3
$(\text{C}_6\text{H}_4)\text{CH.CH} = \text{C}_8\text{H}_7$ ....	— 81·3	+ 16·3

Isomeric primary and secondary residues show different velocities:—

	Value of reaction.	
	Velocity.	Limit.
$\text{Et.CH}_2 = \left. \begin{array}{l} \\ \end{array} \right\} \text{C}_3\text{H}_7$ .....	— 46·1	+ 8·2
$\text{Me.CH} = \left. \begin{array}{l} \\ \end{array} \right\} \text{C}_3\text{H}_7$ .....	— 53·0	+ 8·2
$\text{Me.CH.CH} = \text{C}_3\text{H}_5$ .....	— 80·4	+ 12·3

(III.) *Tertiary Monobasic Acids.*

Series.		Coefficients of combination.	
		Velocity.	Limit.
$C_nH_{2n}O_2$ ..	Trimethyl-acetic acid, $C_5H_{10}O_2$ ....	11·8	113·1
	Dimethyl-ethyl-acetic acid, $C_6H_{12}O_2$ ..	4·8	115·4
$C_nH_{2n-2}O_2$	Ethylcrotonic acid, $C_6H_{10}O_2$ .....	4·8	107·8
$C_nH_{2n-4}O_2$	Sorbic acid, $C_8H_8O_2$ .....	12·9	116·3
$C_nH_{2n-8}O_2$	Benzoic „, $C_7H_6O_2$ .....	13·9	112·9
	Nitrobenzoic acid, $C_7H_5(NO_2)O_2$ ..	40·1	114·3
	Paratoluic „, $C_8H_8O_2$ .....	10·7	119·1
	Cuminic „, $C_{10}H_{12}O_2$ .....	10·1	118·1

Of all the acids, these tertiary acids have the smallest velocities and the highest limits of etherification, the nitro-group showing its peculiar influence. For the corresponding tertiary residues we have :—

	Values of reaction.	
	Velocity.	Limit.
$Me_2.C = C_4H_9$ .....	— 86·5	+ 13·1
$Me_2.Et.C = C_5H_{11}$ .....	— 94·4	+ 15·4
$Me.CH.Et.C = C_5H_9$ .....	— 95·2	+ 7·8
$(C_4H_7).C = C_5H_7$ .....	— 87·1	+ 16·3
$(C_5H_5).C = C_6H_5$ .....	— 86·1	+ 12·9
$(C_5H_4.NO_2).C = C_6H_4.NO_2$ ..	— 59·9	+ 14·3
$(C_5H_4.Me).C = C_7H_7$ .....	— 89·3	+ 19·1
$(C_5H_4.C_3H_7).C = C_9H_{11}$ .....	— 89·9	+ 18·1

The above values show that the decrements of velocities and the increments of limits are the largest compared with the corresponding primary residues :—

	Values of reaction.	
	Velocity.	Limit.
$Et.Me.CH = \text{primary } C_4H_9$ ....	— 64·4	+ 14·8
$Me_3.C = \text{tertiary } C_4H_9$ .....	— 86·5	+ 13·1
$Me.(CH_2)_4 = \text{primary } C_5H_{11}$ ..	— 46·4	+ 8·7
$Et.Me_2.C = \text{tertiary } C_5H_{11}$ ....	— 94·4	+ 15·4
$(C_6H_5)CH_2 = \text{primary } C_7H_7$ ..	— 20·9	+ 15·0
$(C_5H_4)Me.C = \text{tertiary } C_7H_7$ ..	— 89·3	+ 19·1

As regards the influence of the *constant* constituents of organic acids on the formation of ethereal salts, the author shows that it depends on the different order in which the methyl-groups are placed, exactly as in the case of the alcohols. The author compares the coefficients of combination for formic, acetic, propionic, dimethylacetic, and trimethylacetic acids, and shows that with increasing number of methyl-groups the velocity increases, and the limit diminishes.

The author concludes by stating the chief deductions from the above research as to the constitution of the acids.

(1.) On replacing the hydrogen-atom in formic acid, which is connected with the carboxyl-group by a monovalent radicle, the velocity diminishes and the limit increases.

(2.) The smallest changes occur when the remaining affinities of the carbon-atom which is linked to the carboxyl-group, are saturated with hydrogen.

(3.) In the case of the formation of higher primary acids from acetic acid, another diminution of velocity and increase of limit takes place. To 1 atom of carbon in normal saturated acids corresponds an increase of 10.29 of the mol. weight limit (this vol., 384). In other primary acids, the length of the chain of carbon-atoms is only of secondary influence.

(4.) On replacing *two* hydrogen affinities in acetic acid by the affinities of carbon, another and more distinct diminution of velocity and limit of etherification takes place, and this diminution reaches a maximum when

(5.) All three hydrogen-atoms of acetic acid are replaced by monovalent carbon-groups. Here, as well as in case (4) the length of the chain or of the number of affinities has only a small influence.

B. B.

**Halogenated and Hydroxyorganic Acids.** By E. ERLÉNMEYER and C. L. MÜLLER (*Ber.*, 15, 49—50).—When the  $\alpha$ - $\beta$ -dibromobutyric acids obtained by adding bromine to crotonic acid are treated with alcoholic potash, they behave differently to the  $\alpha$ - $\beta$ -dibromopropionic acid, for only one-tenth part of the molecules of the  $\alpha$ - $\beta$ -dibromobutyric acid lose  $\beta$ -bromine and  $\alpha$ -hydrogen; whilst nine-tenths give up  $\alpha$ -bromine and  $\beta$ -hydrogen, thus producing by the  $\beta$ -methylation of the  $\alpha$ - $\beta$ -dibromopropionic acid chiefly  $\beta$ -brominated unsaturated acids, and only small quantities of  $\alpha$ -compounds.

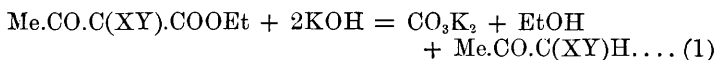
As the potassium salt of the latter is very sparingly soluble in cold absolute alcohol, whilst the two can be readily separated, that of the former is easily soluble.  $\alpha$ -Bromocrotonic acid is also formed when  $\alpha$ -dibromobutyric acid, prepared by brominating  $\alpha$ -monobromobutyric acid, is either heated with water in sealed tubes at 110—120°, or boiled with baryta-water, or digested on a water-bath with water and silver carbonate. It is accompanied by a syrupy acid, smelling like pyruvic acid. By warming  $\alpha$ - $\beta$ -dibromobutyric acid with potassium iodide solution, iodine is set free and crotonic acid is formed. When  $\alpha$ - $\beta$ -dibromobutyric acid is mixed with 10 parts of water and half the molecular weight of sodium carbonate and distilled, propaldehyde and a large quantity of  $\alpha$ -bromopropylene,  $\text{MeCH}:\text{CHBr}$  (which combines with bromine to form  $\text{MeCHBr}.\text{CHBr}_2$ ) pass over, whilst a solution of bromhydroxybutyric acid remains in the retort. This acid may be extracted with ether, and, on evaporation, is left as a syrup. *Calcium bromhydroxybutyrate*,  $(\text{C}_4\text{H}_6\text{BrO}_3)_2\text{Ca}$ , crystallises in slender needles. On treating crotonic acid with hypochlorous acid, a syrupy acid is obtained, yielding a crystalline calcium salt,  $(\text{C}_4\text{H}_6\text{ClO}_3)_2\text{Ca}$ . By decomposing this salt, the acid can be got in wavellite-like crystals (m. p. 53—56°), easily soluble in alcohol, ether, and chloroform, sparingly soluble in carbon bisulphide and light petroleum.

D. A. L.

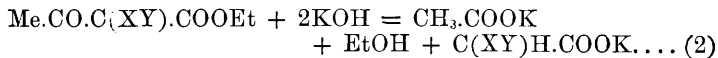
**Normal  $\alpha$ -Amidovaleric Acid.** By V. JUSTIN (*Bull. Soc. Chim.* [2], 37, 3—4).—Valeric acid is converted into the bromo-derivative, and the latter is heated with concentrated aqueous ammonia in sealed tubes at  $130^\circ$  for six hours. The product is then heated with lead hydroxide, filtered, the excess of lead removed by hydrogen sulphide, the solution evaporated, and the crystals purified by washing with alcohol and ether, and finally crystallising from alcohol. Normal  $\alpha$ -amidovaleric acid,  $C_5H_{11}NO_2$ , thus obtained, forms long colourless prismatic needles, white when dry, very soluble in water, slightly soluble in alcohol, and almost insoluble in ether. It sublimes without melting. C. H. B.

**Propyl-derivatives and Decomposition-products of Ethylic Acetoacetate.** By B. S. BURTON (*Amer. Chem. J.*, 3, 385—395).—*Ethyl propylacetoacetate*,  $C_9H_{16}O_3 = Me.CO.CHPr^a.COOEt$ , prepared, according to Conrad and Limprich's process (*Abstr.*, 1878, 781), by adding ethylic acetoacetate (152.7 g.) and propyl iodide (206 g.) to a solution of 7 g. sodium in 270 g. absolute alcohol, is a clear limpid fragrant liquid, having a density of 0.981 at  $0^\circ$  compared with water at  $4^\circ$ , and boiling at  $205-210^\circ$ . *Ethyl dipropylacetoacetate*,  $C_{12}H_{22}O_3 = Me.CO.CPr^a_2.COOEt$ , resembles the preceding in appearance and odour, has a density of 0.585 at  $0^\circ$  (compared with water at  $4^\circ$ ), and boils at  $235-236^\circ$ .

*Saponification of the Ethers above described.*—The researches of Geuther and of Frankland and Duppa have shown that the ethylic ethers of acetoacetic acid and its alkyl-derivatives are resolved by the action of alkalis into carbonic acid, ethyl alcohol, and a ketone, according to the following general equation, in which X and Y denote alcohol-radicles or alkyls:—



and it has been further shown by Wislicenus that this reaction is accompanied by another, resulting in the formation of acetic acid or an alkyl-derivative thereof, according to the equation—



The relative amounts of ketone and organic acid thus formed depend, not only on the substituted radicle, but also on the concentration of the alkali employed, the amount of the ketonic ether split up into two molecules of organic acid (eq. 2) being greater as the alkali used is more concentrated, whereas the quantities of carbonic acid and ketone produced (eq. 1) are greater as the alkali is more dilute. The following table exhibits a comparison of the decomposition-products of the ethylic ethers of mono- and di-propylacetoacetic acid with those of the methyl- and ethyl-derivatives, as given by Wislicenus (*Annalen*, 190, 280):—

	Methyl.	Ethyl.	Propyl.	Dimethyl.	Diethyl.	Dipropyl.
With 10 per cent. KOH sol.						
Ketone and CO <sub>2</sub> ..	86·28	91·52	71·68	91·73	54·15	34·24
Organic salts ....	13·70	8·75	25·78	7·46	42·50	58·76
With 20 per cent. KOH sol.						
Ketone and CO <sub>2</sub> ..	68·16	73·44	55·16	80·02	30·86	12·22
Organic salts ....	31·30	23·75	44·41	19·96	69·46	86·69

These numbers show that ethylic monopropylacetoacetate, like the other mono-derivatives, undergoes, both with dilute and with concentrated potash-solution, a decomposition in which ketone and carbonic acid preponderate; whereas ethylic dipropylacetoacetate yields, both with dilute and with concentrated alkali, a product consisting chiefly of organic salts, this mode of decomposition being especially remarkable when compared with that of the methyl-derivative.

*Dipropylacetic acid*,  $C_8H_{16}O_2 = (C_3H_7)_2CH.COOH$ , prepared by the action of potash on ethylic dipropylacetoacetate, is a colourless, oily, slightly acid liquid, sparingly soluble in water, and having the characteristic odour of the higher fatty acids. Sp. gr. = 0·9215 at 0°; (water at 4° = 1); b. p. 219·5°. The sodium salt gives precipitates with silver, copper, and lead salts. The barium salt is easily soluble.

The *ethylic salt* is a colourless limpid liquid, having a pleasant odour, and boiling at 183°.

The isomeric octoic or caprylic acid,  $CHMe_2.(CH_2)_4.COOH$ , which occurs as a glyceride in cows' milk and cocoa-nut oil, and is produced by oxidation of iso-octyl alcohol (from Heracleum oil), is solid at ordinary temperatures, melts at 16—17°, boils at 235—237°, and forms a sparingly soluble barium salt. Another iso-octoic acid,  $CHMe_2(CH_2)_2.CHMe.COOH$ , formed by oxidation of the corresponding alcohol from di-isobutyl, is an oily liquid, which boils at 218—220°, and does not solidify at -17°. A fourth iso-octoic acid,  $CMc_3.CH_2.CHMe.COOH$ , which Butlerow obtained by oxidation of di-isobutylene, is also liquid at ordinary temperatures, and distills between 205° and 218°; for the most part at 215° (Abstr., 1878, p. 781).

*Dipropyl-acetone or Methyl-dipropylmethyl Ketone,*



is contained in the oily layer which separates in the saponification of ethylic dipropylacetoacetate, and may be purified by drying with calcium chloride and fractional distillation. It is thus obtained as a colourless limpid liquid, having a pleasant ketonic odour, and boiling at 173—174°. It does not appear to form a crystallisable compound with acid sodium sulphite.

*Action of Sodium-amalgam on Ethylic Dipropylacetoacetate.*—This reaction was expected to yield dipropyl-beta-hydroxybutyric acid, just as diethyl-beta-hydroxybutyric acid is obtained from ethylic diethyl-

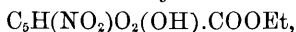


acetoacetate. Experiment showed, however, that this is not the case, the dipropyl-acid not being formed, even when the free alkali in the liquid was neutralised from time to time with sulphuric acid. When the action was completed and the liquid again neutralised, an oily liquid separated, which proved to be dipropylacetone; and on removing this, the remaining liquid was found to contain acetic and dipropyl-acetic acids.

The remainder of the paper is occupied with the description of unsuccessful attempts to obtain triethylacetic acid by the action of phosphorus pentachloride, hydriodic acid, or hydrobromic acid on the sodium salt of diethyl-beta-hydroxybutyric acid, the product in all cases being diethylacetic acid. H. W.

**Meconic Acid.** By H. Ost (*J. pr. Chem.* [2], **23**, 439—443 (see also this Journal, **36**, 708).—*Triethyl meconate*,  $C_5HO_2(OEt)(COOEt)_2$ , is obtained by acting on silver diethyl meconate with ethyl iodide; it crystallises from alcohol in needles (m. p.  $61^\circ$ ), and yields no coloration with ferric chloride.

*Derivatives of Comenic Acid.*—*Ethyl nitrocomenate*,



is obtained by nitrating ethyl comenate; it forms yellow needles, and yields a red coloration with ferric chloride. On reduction with tin and hydrochloric acid, it yields amidocomenic acid, which crystallises with 1 mol.  $H_2O$  in colourless needles; it imparts a deep-blue colour to ferric chloride solutions. When boiled with baryta-water, it yields hydroxycomenic acid,  $C_5HO_2(OH)_2COOH$ , which crystallises with 3 mols.  $H_2O$  in needles, and with 1 mol.  $H_2O$  in small prisms. Ammonium hydroxycomenate is sparingly soluble in water; the ethyl salt is a crystalline substance, which, by ammonia, is converted into comenamide,  $C_5H_2O_2(OH).CONH_2$ , isomeric with comenamic acid. Hydroxycomenic acid is also obtained by boiling bromocomenic acid with hydrochloric or hydrobromic acid. When treated with bromine and water, it yields an acid having the formula  $C_5H_3BrO_5 + H_2O$ , also carbonic anhydride. Bromopyromeconic acid behaves like bromocomenic acid, and is easily converted into hydroxycomenic acid,  $C_5H_4O_4$ , which, when treated with bromine and water, yields an acid  $C_4H_3BrO_5 + H_2O$ , and carbonic anhydride.

*Pyromecazonic acid*,  $C_5H_5NO_3$  (*loc. cit.*), can be obtained by reducing hydroxypyromecazonic acid with hydriodic acid; it forms a diacetic derivative,  $C_5H_3\bar{A}C_2NO_3$ , and with bromine a monobromo-derivative,  $C_5H_4BrNO_3$ , the hydrochloride of which is decomposed by water.

*Pyromecazone*,  $C_5H_3NO_3$ , is obtained by adding concentrated nitric acid to an ethereal solution of pyromecazonic acid. It crystallises from methyl and ethyl alcohols in colourless needles containing a molecule of the respective alcohols; it is insoluble in ether, soluble in water. Its aqueous solutions give no coloration with ferric chloride, and stain the skin violet. Pyromecazone is also obtained by acting on a solution of pyromecazonic acid in glacial acetic acid, which, by further addition of nitric acid, is converted into nitro-pyromecazone,  $C_5H_2(NO_2)NO_3 + H_2O$ . The aqueous solution of this compound,

when heated at 30—40°, yields carbonic anhydride and nitropyromecazonic acid,  $C_5H_4(NO_2)NO_2$ , which crystallises from water in golden-yellow leaflets, and gives a red coloration with ferric chloride.

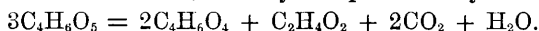
P. P. B.

**Occurrence of Succinic Acid in an Incrustation on the Bark of "Morus Alba."** By G. GOLDSCHMIDT (*Monatsh. Chem.*, **3**, 136—138).—The author had often observed on the stems of mulberry-trees, both young and old, the exudation of a liquid, which dried up to crystalline crusts, especially on the side exposed to the wind. This liquid, which had a saline taste, was found to consist of a solution of calcium succinate,  $C_4H_4O_2Ca$ , which, after several recrystallisations with the aid of animal charcoal, melted at 180°, and was converted by distillation into the anhydride melting at 160°. The liquid also contained a small quantity of calcium carbonate.

The occurrence of exudations on mulberry-trees was observed long ago by Klaproth, who regarded them as consisting of the calcium salt of an acid which he called "Maulbeerholzssäure," and similar observations were afterwards made by Landerer. Gmelin (*Handbook*, Engl. Ed., **8**, 109) suggests that the acid found by these chemists was nothing but succinic acid, a suggestion which is corroborated by the observations above mentioned.

The occurrence of succinic acid in the juices of a large number of herbs has long been noticed; but it has not hitherto been found in liquids exuding from trees; and this circumstance, together with the observation that on all parts of the bark where the exudation occurred, a brown humus-like substance was also found, induced the author to think that the succinic acid in this case, might perhaps be, not a physiological secretion, but the product of a pathological process.

To throw light on this question, he submitted the humus-like substance to the examination of Professor Wiesner, who found it to consist of dried plasmodia and sporiferous receptacles of a myxomices, most probably a species of *Aethalium*. The plasmodia of myxomicetes are, according to Reinke (*Studien über das Protoplasma*), very rich in mineral substance containing a large proportion of lime. Succinic acid was not found in them by Reinke. The occurrence of the succinic acid is perhaps due to a fermentation process, in consequence of which the malic acid occurring in the juices of the mulberry-tree (Gmelin, **10**, 206) is converted into succinic acid, a metamorphosis, which, according to Fitz (*Ber.*, **12**, 481) takes place somewhat readily in schizomycetic fermentations, and may be represented by the equation:—



H. W.

**Decomposition of Racemic Acid.** By E. JUNGFLEISCH (*J. Pharm. Chim.* [5], **5**, 346—352).—Pasteur's method for the decomposition of racemic acid by crystallising a concentrated solution of sodium ammonium racemate and separating the crystals by actual examination for the hemihedral faces, is one of great labour, since a large number of crystals must be examined for the separation of a small quantity of acid, as many of them are devoid of the hemihedral faces. This examination may

be replaced by a chemical reaction. A small portion of the crystal is dissolved in a drop of water, and the solution divided into two parts; one portion is treated with a solution of right-handed calcium tartrate, and the other with left-handed calcium tartrate; a precipitate of calcium racemate is formed by this reagent with the sodium ammonium tartrate of opposite rotatory power of itself. This method is particularly applicable to the examination of large crystals.

Gernez, however, has shown (*Compt. rend.*, **63**, 843) that when a supersaturated solution of sodium ammonium racemate is treated with a crystal of the right-handed tartrate of the same bases, only right-handed crystals form, and *vice versa*; but the objections to this method are that if only slightly concentrated solutions are used, several operations are required to obtain any quantity of the acid, whereas by using highly concentrated solutions, the salt of opposite rotatory power is apt to crystallise with the other.

The author modifies this method by treating a concentrated solution of the racemate simultaneously with crystals of opposite rotatory power.

Ammonium sodium racemate is prepared by neutralising equal weights of racemic acid with sodium carbonate and ammonia, and mixing the solutions; and the mixture is then concentrated to such a strength that 1 litre will deposit 150—160 grams of crystals. The amount of concentration depends on the temperature of the laboratory, and may be determined by taking the density from time to time (the density varies from 1.24—1.28); or better by placing in the solution a glass bulb, which will float in a liquid of the required density, and evaporating the solution until the bulb floats. The ammonia which escapes during the evaporation must be replaced at the end of the operation in such quantity as to give the solution a slightly alkaline reaction. This solution is poured into a crystallising dish with ground edges, holding from 1 to 2 litres, and covered with a glass, which forms a tight joint. The steam then condenses on the cover-glass, and moistens the edges of the dish, and by means of the capillarity a sort of hydraulic joint is formed and evaporation prevented. The vessel is placed in a room of constant temperature and left to cool; when cool, a crystal of right-handed sodium ammonium tartrate, washed in a stream of water and still wet, is gently dropped into the solution on the right side, and a crystal of the left-handed salt on the left. These crystals being moist, dilute the solution directly surrounding them, and grow slowly, attaining their maximum size in two or three days, when each has been increased by the salt of its own rotatory power. The mother-liquor may be concentrated, and the operation repeated a second and third time, and a fresh quantity of the racemate dissolved in it, the solution brought to the required density and crystallised as before.

The separate crystals are then purified by recrystallisation.

At 15°, right-handed sodium ammonium tartrate is less soluble in water than the left-handed salt, and not equally soluble as is generally admitted; this may account for the fact that some racemates on crystallising separate into right- and left-handed tartrates, whilst others crystallise unaltered.

In two cases, on allowing the concentrated solution of the double racemate to cool out of contact with the air, needle-shaped crystals separated throughout the solution; and on placing in it crystals of the right- and left-handed tartrates, the needles disappeared, whilst the other crystals increased at their expense. These crystals may be a particular form of the two tartrates, or another hydrate of the two salts, or as is most probable, the double racemate crystallising without decomposition. Owing to the rapidity with which they disappear, the author has been unable to examine them.

L. T. O'S.

**Ammoniacal Citrates.** By E. LANDRIN (*Ann. Chim. Phys.* [5], 25, 233—257).—It is well known that many metallic oxides and citrates, insoluble in water, are soluble in the alkaline citrates, even in the presence of reagents, which under ordinary conditions precipitate these oxides. This phenomenon has been made the basis of a quantitative method for the determination of phosphoric acid. Some years ago, Spiller (*Pharm. Journ.*, 1858) carried on a series of investigations, in order to study the influence of citric acid in preventing the precipitation of the metallic oxides, and arrived at the general result that the neutral citrates possess the property of combining with other salts to form a class of compounds of the general formula  $M'_3C_6H_5O_7 + 3M'SO_4$ , in which sulphuric acid may be replaced by carbonic, chromic, or boracic acids. For instance, solutions of these compounds are not precipitated by barium nitrate until a slight excess of sodium sulphate is present. Lebaigne, however, considers that these phenomena are due to an interchange between the acids and bases, which is stable only so long as the citrate liberated in the nascent state is soluble, and thus the peculiar characteristics of the acids and bases present become apparent when the nascent citrate has saturated the alkaline citrate, viz., when the precipitant is in excess of the alkaline citrate. Further, the insoluble citrates are dissolved in the alkaline citrate in definite proportions, and citric acid being tribasic can saturate not only three equivalents of the same, but also of different bases to form soluble salts.

In order to decide between these views, the author has taken up the question, and has arrived at results in accordance with those of Lebaigne, i.e., citrates insoluble in water dissolve in alkaline citrates, with formation of double salts of the composition  $M_2M'C_6H_5O_7$ , in which M is an alkali-metal, and M' a metal belonging to some other class.

This result receives support from the following experiments: if barium carbonate is gradually added to citric acid saturated with ammonia until one equivalent of acid and baryta are present, a clear solution is obtained, from which, on cooling, normal barium citrate separates out. The supernatant liquid contains in solution a double ammonium barium citrate. Analogous phenomena were observed with the oxides of calcium, strontium, lead, and cadmium. Again, if aluminium hydroxide be dissolved in ammonium citrate, and the solution evaporated over sulphuric acid, white crystals of a double ammonium aluminium citrate,  $3C_6H_5O_7(NH_4)_2H + [C_6H_5O_7(NH_4)_2]_3Al_2 + 6H_2O$ , will separate out. A similar iron salt was obtained, a solution of which gives no precipitate with succinic and benzoic acids, no color-

tion with potassium thiocyanate, and no precipitate but only a green coloration with potassium ferrocyanide. The author also prepared and analysed analogous double citrates of ammonium and magnesium, manganese, nickel, cobalt, zinc, copper, and mercury, but was unable to obtain salts of antimony, bismuth, tin, or silver. V. H. V.

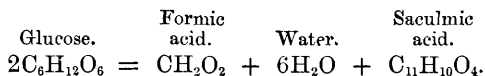
**Saculmin Compounds.** By F. SESTINI (*Landw. Versuchs.-Stat.*, 27, 163—175).—Saculmic acid is prepared by treating saculmin with a cold solution of potash or soda (Abstr., 1880, 538, 865), when it swells up and partially dissolves, forming a fluid of intense brown colour; this carefully filtered and saturated with hydrochloric or sulphuric acid, deposits a rich brown precipitate, which is collected on a filter and washed until the wash-water is free from acid; it is then partially dried between blotting paper, and completely in a desiccator in presence of sulphuric acid; it cannot be dried at 100°, as it loses some of its properties, notably its solubility in alcohol.

Saculmic acid, prepared in this way, appears as shining black fragments, sparingly soluble in water, more so in dilute alcohol, easily soluble in alcohol at 90°; it is very difficult of solution in absolute alcohol, and insoluble in ether; precipitation and reprecipitation from solution in alcohol, is the best method for obtaining the substance in a pure state; while moist, it redissolves freely in alcohol; the solution is reddish-brown in reflected light, ruby-coloured by transmitted light; acid to test-paper, and yields a brown flocculent precipitate to silver nitrate, barium hydroxide, hydrochloric acid, and sodium chloride.

Analyses were made of saculmic acid obtained from cane-sugar and from glucose, with the following results:—

	Cane-sugar.		Glucose.	
	1.	2.	1.	2.
Combustible matter after deduction of ash, gram	0.1684	0.2648	0.3303	0.2437
CO <sub>2</sub> obtained..... „	0.3938	0.6183	0.7690	0.5711
H <sub>2</sub> O obtained..... „	0.0756	0.1143	0.1308	0.0966
Carbon..... per cent.	63.78	63.68	63.50	63.91
Hydrogen .... „	4.98	4.79	4.40	4.40

These results correspond nearly with the formula C<sub>11</sub>H<sub>10</sub>O<sub>4</sub>, which agrees with the author's previous observations, that formic acid is disengaged during the formation of saculmin from glucose. When 1 mol. of formic acid and 6 mols. of water are taken from 2 mols. of glucose, saculmic acid remains:—

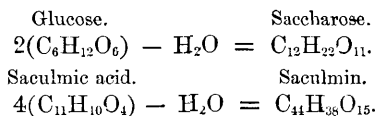


The same formula is deducible from the saculmates, of which the author gave the analyses of the silver and barium salts.

Saculmin, when treated repeatedly with a cold solution of potash or soda of 5 per cent., and the brown liquid heated on a water-bath, yields a brown deposit, which the author provisionally calls

saculmious acid; the residue undissolved by the reagent he calls saculmin, and finds it to differ in composition from saculmic acid, the results nearly agreeing with the formula  $C_{44}H_{38}O_{15}$ .

Finally, the author considers saculmin to be the anhydride of saculmic acid, in the same manner as saccharose is an anhydride of glucose.



J. F.

**Action of Halogenated Organic Radicles on Potassium-pyrroline.** By CIAMICIAN and DENNSTEDT (*Gazzetta*, 1882, 84).—*Ethyl chlorocarbonate* acts violently on potassium-pyrroline at the ordinary temperature, but the action may be moderated by adding a quantity of anhydrous ether equal to twice the volume of the chlorocarbonate. Even then the mixture ultimately becomes heated to ebullition, but to complete the reaction, which is represented by the equation,  $C_4H_4NK + ClCOOEt = KCl + C_4H_4N.COEOEt$ , the mixture must be heated on the water-bath. On subsequently distilling off the ether, together with the excess of ethyl chlorocarbonate, at the heat of the water-bath, treating the residue with water, drying the oil thereby separated with calcium chloride, and submitting it to fractional distillation, a colourless liquid is obtained, heavier than water, having an etheric odour (b. p.  $180^\circ$  under 770 mm. pressure), and giving by analysis 60.23 per cent. C and 6.65 H, leading to the formula  $C_7H_8NO_2$ , which requires 60.43 C and 6.43 H. This compound, boiled with caustic potash or baryta, is resolved into pyrroline, carbonic anhydride and ammonia, and may therefore be regarded as tetrene-urethane or ethyltetrene-carbonate,  $EtO.CO.N:C_4H_4$ , the bivalent radicle  $C_4H_4$  being called *tetrene*. On heating this substance with ammonia for four hours in sealed tubes at  $110^\circ$ , a liquid is obtained which, when evaporated, yields a new crystallised substance melting at about  $167^\circ$ , and having the composition of tetrene-carbamide or tetrene-urea,  $C_6H_4:N.CONH_2$ , isomeric with carbo-pyrrolamide.

The authors have begun to study the action of ethylene chloride on potassium pyrroline, which takes place very quickly, whereas the chlorides of methylene and ethylidene have little or no action on that compound.

H. W.

**Aluminium Chloride and Monobromobenzene.** By O. v. DUMREICHER (*Ber.*, 15, 33).—When warmed together, these bodies yield dibromobenzene (liquid as well as solid [m. p.  $89^\circ$ ]), a liquid (b. p.  $80^\circ$ ), probably benzene, and a high-boiling oil, hydrochloric acid being freely evolved.

D. A. L.

**Tetrabromobenzene (m. p.  $175^\circ$ ).** By R. MEYER (*Ber.*, 15, 46—48).—The author has repeated Kekulé's (*Annalen*, 137, 169) and Riche and Bérard's (*ibid.*, 133, 51) experiment. By heating 10 grams paradibromobenzene with 20 grams bromine in sealed tubes at  $150^\circ$ ,

as long as hydrobromic acid is evolved, and in the same way treating 8.5 grams nitrobenzene with 27 grams bromine for a day at 250°, a tetrabromobenzene was obtained, crystallising in white needles (m. p. 175°).  
D. A. L.

### Conduct of Nitrometaxylene towards Oxidising Agents.

By I. REMSEN and M. KUHARA (*Amer. Chem. J.*, **3**, 424—433).—Nitroxylene prepared according to Beilstein and Kruger's method (*Annalen*, **144**, 167), by the action of the strongest nitric acid on commercial xylene (previously freed from paraxylene by prolonged boiling with dilute nitric acid) was converted, by oxidation with chromic acid mixture, into nitrotoluic acid,  $C_6H_3(NO_2)Me.COOH$ , which, after purification by conversion into calcium salt, separation therefrom, recrystallisation from water, and sublimation, melted at 214°. This nitro-acid was reduced by tin and hydrochloric acid to the corresponding amido-acid; the latter was converted by the action of nitrous acid into the diazo-acid; and this, by boiling with water into the corresponding hydroxytoluic acid, which, after purification by boiling with bone-black, crystallised in fine lustrous silky needles, slightly soluble in cold, freely in boiling water, forming a solution not coloured by ferric chloride; easily soluble in cold alcohol and ether, insoluble in carbon bisulphide; melting in the air-dried state at 148.5—149.5° (corr.), and after drying at 100°, at 174° (corr.). The air-dried crystals gave by analysis numbers agreeing with the formula  $C_7H_5O_3 + \frac{1}{2}H_2O$ , the water of crystallisation being given off at 100°.

The composition and properties of this acid show that it is identical with that which Remsen and Iles obtained (*Ber.*, **11**, 888) by fusing sulphamine-toluic acid with potash, and with the *orthohomoparahydroxybenzoic acid* which Tiemann and Schotten prepared by introducing the aldehyde-group into ortho-cresol, and oxidising the resulting aldehyde (*ibid.*, 767). Its constitution is therefore represented by the

formula  $C_6H_3(OH)(Me)(COOH)$ , and the nitrotoluic acid, from which it is prepared, has a similar constitution, viz.  $[NO_2:Me:COOH = 1:2:4]$ . The formation of a hydroxytoluic acid of this constitution by the oxidation of nitrometatoluene, affords an additional illustration of the power possessed by negative radicles, Cl, Br,  $NO_2$  (previously noticed by Remsen: see p. 186 of this volume) of protecting contiguous hydrocarbon residues from the action of oxidising agents. In the present instance the methyl-group, standing in the *para*-position to the  $NO_2$  is oxidised by the chromic acid, while the methyl in the ortho-position remains intact. In like manner, when xylene is treated with sulphuric acid, the chief product is a sulphonic acid similar in constitution to the nitroxylene above considered, and convertible by oxidation and subsequent fusion with potassium hydroxide, into a hydroxy-acid identical with that which is obtained from the nitroxylene.

*Transformation of Amidotoluic Acid into Chloro- and Bromo-metatoluic Acids.*—The diazo-compound obtained from amidometatoluic acid is converted by boiling with strong hydrochloric acid into a chlorotoluic acid,  $C_6H_3Cl(Me)(COOH)$ , identical with the so-called parachlorotoluic acid which Vollrath obtained by oxidising chloro-

xylene with chromic acid (*Annalen*, **144**, 266). After purification by boiling with bone-black and crystallisation from alcohol, it forms groups of slender nearly colourless needles, slightly soluble in cold, easily in hot alcohol; melting at  $204^{\circ}$  (corr.), and easily subliming. The corresponding bromotoluic acid, prepared in like manner, is almost insoluble in water, either hot or cold, slightly soluble in cold, easily in hot alcohol, and separates therefrom in white crystals melting at  $208-209^{\circ}$  (corr.). It is identical with the bromotoluic acid which Fittig, Ahrens, and Mattheides obtained by the oxidation of bromoxylene (*Annalen*, **147**, 15). In the formation of these halogen-toluic acids from chloro- and bromo-xylene in the manner just described, it is likewise seen that the ortho-methyl group is protected while the para-group is oxidised.

H. W.

**Preparation of Cymene: Action of Zinc-dust on Terebenthene Dichloride.** By L. NAUDIN (*Bull. Soc. Chim.* [2], **37**, 110—111).—Pure terebenthene cooled to  $-15^{\circ}$  will absorb two equivalents of dry chlorine without sensible evolution of hydrochloric acid, forming the compound  $C_{10}H_{16}Cl_2$ , which on gentle heating splits up into hydrochloric acid and cymene. The latter may be rectified over sodium. Or dry chlorine may be passed into terebenthene containing 4 per cent. phosphorus trichloride, at a temperature of  $25^{\circ}$ : hydrochloric acid is evolved regularly, and the product is washed with water, and dried over calcium chloride. In this reaction the phosphorus trichloride is first converted into the pentachloride, and this gives up two atoms of chlorine to the terebenthene, forming the chloride  $C_{10}H_{16}Cl_2$ , which then splits up. The yield of cymene is about 75 per cent.

Terebenthene dichloride,  $C_{10}H_{16}Cl_2$ , is violently decomposed by traces of zinc-dust at  $100^{\circ}$ , with evolution of large quantities of hydrochloric acid and formation of cymene and diterebenthene. No tetraterebenthene is produced.

C. H. B.

**Action of Phosgene on Diazoamido-Derivatives.** By A. SARAUW (*Ber.*, **15**, 42—46).—In a recent communication (this vol., 507) the author has shown that in diazobenzeneparatoluide the free imido-hydrogen occupies a position adjacent to the toluene-group. He has now extended his experiments to diazobenzeneamidobenzoic acids, &c., in order to characterise the position which the imido-hydrogen generally occupies in mixed diazoamido-derivatives.

*Phosgene and Diazobenzenemetamidobenzoic Acid.*—The acid was prepared by mixing an aqueous solution of azobenzoic nitrate with 2 mols. aniline. The action of the phosgene on the acid itself being too violent, and the acid being only slightly soluble in ether, benzene, and chloroform, the phosgene was condensed in benzene, and 2 mols. of finely powdered diazobenzeneamidobenzoic acid were added in small quantities at a time to the calculated quantity of this solution of phosgene. After half an hour, the benzene was removed by the pump and the residue decomposed with water. The products were *phenol*, *hydroxybenzoic acid* (m. p.  $199^{\circ}$ ), and an indefinite acid substance insoluble in water.



The acidity of the latter product and the non-formation of carbanilide, point to the fact that the phosgene has acted on the amido-acid residue, and hence the formula of diazobenzenemetamidobenzoic acid would be  $\text{Ph.N}_2.\text{NH.C}_2\text{H}_4.\text{COOH}$ .

*Carbonylamidobenzoic acid* (which the author hoped to isolate in the above reaction) can be prepared by the action of phosgene on metamidobenzoic acid suspended in benzene. It is a white powder quite insoluble in water and nearly so in alcohol and benzene, but dissolves easily in alkalis and ammonia, and is reprecipitated by acids (comp. Griess, *Annalen*, **172**, 169).

The *ammonium salt* is stable in solution only; on evaporation ammonia passes off, and the free acid is left. The *lead salt* is a white precipitate; the *silver salt* is also white, but becomes discoloured on exposure to light.

*Phosgene and Diazobenzeneparabromanilide*.—The latter was prepared by mixing an aqueous solution of parabromodiazobenzene nitrate with 2 mols. aniline. It is easily soluble in benzene or ether. A stream of phosgene is passed through a benzene solution of this body until the mass becomes dark coloured. The benzene is separated from the insoluble body, probably a carbamide,  $\text{CO}(\text{NC}_6\text{H}_4\text{Br.N}_2.\text{Ph})_2$ , which is decomposed by warming with water, yielding *phenol* and *dibromocarbanilide* (comp. Otto, *Ber.*, **11**, 409), sparingly soluble in alcohol, insoluble in water. It does not melt at  $240^\circ$ , but a white sublimate forms at  $225^\circ$ . The formula for diazobenzeneparabromanilide is therefore  $\text{Ph.N}_2.\text{NH.C}_6\text{H}_4\text{Br}$ . Dibromocarbanilide is also obtained on saturating a chloroform solution of parabromaniline with phosgene. From these experiments and results the author infers that in mixed diazoamido-derivatives the imido-group is generally combined with the negative aromatic residue. It is remarkable that dilute solutions of the phenols (with the exception of that from ditolyldiazobenzene-carbamide) obtained by decomposing the above carbamides, do not show the characteristic phenol reaction with ferric chloride.

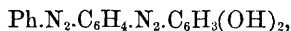
D. A. L.

**Azo Colouring Matters.** By O. WALLACH (*Ber.*, **15**, 22—29).—By the combination of diazo-compounds with phenols, a whole series of bodies have been obtained of the constitution represented by the general formula  $\text{RN:NPh}$ , in which R is a monad aromatic radical, and Ph a monad phenol residue. Bodies of this sort containing one phenol and one diazo-group, are very numerous, whilst of those containing more than one azo-group combined with one phenol, there are only few (*ibid.*, **11**, 627, and **12**, 227), and there is only one compound known in which different azo-residues are combined with one phenol residue (Griess, *ibid.*, **11**, 628). The author finds that the diatomic phenols, such as resorcinol and orcinol, are capable of uniting with two either similar or dissimilar azo-residues, forming bodies of the general formula  $\text{R.N}_2.\text{C}_6\text{H}_2(\text{OH})_2.\text{N}_2.\text{R}'$ , in which R' may be like or unlike R. They are prepared by adding a molecule of a diazo-compound to an alkaline solution of the monazo-derivative of the phenol, and appear to form several isomerides. For example: if diazonaphthalene acts on azobenzeneresorcinol,  $\text{PhN:N.C}_6\text{H}_3(\text{OH})_2$ , a body of the formula  $\text{Ph.N}_2.\text{C}_6\text{H}_2(\text{OH})_2.\text{N}_2.\text{C}_{10}\text{H}_7$ , is obtained, and if diazobenzene

acts on azonaphthaleneresorcinol, the product is similar in constitution: whence arises the question, is it indifferent which of the azo-groups is first combined with the phenol? In order to distinguish by name these possible isomerides, the author suggests that the name of the azo-group first introduced be placed *before*, and the name of the azo-group last introduced *after* the phenol, so that in the cases cited above the first body would be azobenzeneresorcinolazonaphthalene, the second azonaphthaleneresorcinolazobenzene; and further to distinguish these bodies from ordinary azo-compounds, they can be called disazo, trisazo, &c., compounds. There is still another possibility of isomerism in these bodies, *e.g.*, azobenzeneresorcinolazobenzene—



is apparently isomeric with the body (produced by introducing the diazo-derivative of amidoazobenzene into resorcinol)—



azonazobenzeneresorcinol. The author proposes to distinguish these bodies by the names secondary, tertiary, &c., azo-compounds.

By the action of 1 mol. diazobenzene chloride on an alkaline solution of azobenzeneresorcinol prepared by Typke's method (*Ber.*, **10**, 1576), a mixture of two bodies is obtained. They both crystallise in red-brown needles, but differ in their solubility in chloroform. The more soluble (m. p.  $215^\circ$ ) dissolves in soda and concentrated sulphuric acid with a red colour; the less soluble (m. p.  $225^\circ$ ) dissolves in the latter reagent with an indigo-blue colour, and is almost insoluble in soda. In order to see if these bodies were disazo or secondary azo compounds, he tried the action of the diazo-derivative of amidoazobenzene on resorcinol. A reddish-brown product is obtained, of which part is soluble in alcohol, and dissolves in alkalis and concentrated sulphuric acid with a carmine-red colour, and part insoluble in alcohol, slightly soluble in alkalis, and in concentrated sulphuric acid gives rise to a deep blue colour. Azotolueneresorcinol is easily prepared from paratoluidine in a manner similar to the corresponding benzene body. It forms bright red needles (m. p.  $187^\circ$ ) easily soluble in cold alcohol and in soda, with an orange-yellow colour. Diazobenzene chloride acts readily on this body in alkaline solutions, the liquid becomes claret-coloured, and acids precipitate a brown body from it: this also is a mixture, and is separated by cold chloroform into two substances, the one easily soluble,  $\alpha$ , the second only slightly so,  $\beta$ .  $\alpha$  crystallises in brown needles (m. p.  $189^\circ$ );  $\beta$  is precipitated by alcohol from its solution in hot chloroform as a voluminous golden-yellow mass of fine microscopic crystals (m. p. above  $200^\circ$ ); both dissolve in soda with a carmine-red colour and in concentrated sulphuric acid with a red colour. From the analyses, they are apparently isomeric, have the formula  $\text{C}_7\text{H}_7.\text{N}_2.\text{C}_6\text{H}_2(\text{OH})_2.\text{N}_2.\text{Ph}$ , and are therefore azotolueneresorcinolazobenzene. In order to solve the question propounded above, the action of paradiazotoluene chloride on azobenzeneresorcinol was tried and the products were to all appearances identical with  $\alpha$  and  $\beta$ . The author has not yet succeeded in obtaining diazotolueneresorcinol ( $\text{C}_7\text{H}_7.\text{N}_2)_2\text{C}_6\text{H}_2(\text{OH})_2$  by the action of the

diazo-derivative of paratoluidine on paraazotolueneresorcinol; this negative result is not compatible with his views of the constitution of diazo-compounds. Azoxyleneresorcinol,  $C_6H_3Me_2.N_2.C_6H_3(OH)_2$ , is best prepared by adding 1 mol. sodium acetate solution to a dilute aqueous solution of a mixture of 1 mol. diazoxylenechloride and 1 mol. resorcinol. Azoxyleneresorcinol separates out; it is completely soluble in soda, and crystallises from alcohol in red needles. Diazonaphthaleneresorcinol,  $C_{10}H_7.N_2.C_6H_3(OH)_2$ , is soluble in soda, and crystallises from alcohol in scarlet-red needles (m. p. about  $200^\circ$ ). By treating an alkaline solution of this body with diazobenzene chloride, and then with acid, a dark-coloured substance separates, which after purification has an iridescent green lustre (m. p.  $156^\circ$ ), is soluble in concentrated sulphuric acid with blue colour. The body is *azonaphthaleneresorcinolazobenzene*,  $C_{10}H_7.N_2.C_6H_2(OH)_2.N_2.Ph$ , a body of similar properties (*azobenzeneresorcinolazonaphthalene*) melting at  $153-155^\circ$ , is obtained by the action of azobenzeneresorcinol on diazonaphthalene. Neither of these disazo-bodies have as yet been further examined. Almost all the above-mentioned bodies are insoluble in water; soluble colouring matters can, however, be obtained by acting on the amidosulphonic or the diazosulphanilic acids with the azophenols.

Corresponding reactions take place with orcinol-derivatives, and the resulting products are of a brighter and better colour.

D. A. L.

**Action of Heat on Thioformanilide.** By W. W. J. NICOL (*Proc. Roy. Soc. Edin.*, **11**, 199—202).—When thioformanilide is heated to  $180^\circ$ , it is decomposed into sulphuretted hydrogen and a body,  $C_{14}H_{12}N_2S$ , derived from two mols. thioformanilide, less 1 mol.  $H_2S$ . As the constitutional formula of thioformanilide is unknown, no certain formula can as yet be assigned to the new compound.

E. W. P.

**Phenol Hydrate.** By W. ALEXEJEFF (*Jour. Russ. Chem. Soc.*, 1882, 110).—All attempts to obtain such a compound were in vain. The product, described by Lowe as "hydrate of carboic acid," was proved to be a mixture of phenol and water.

B. B.

**Conversion of Paramidophenol into Tri- and Tetra-chloroquinone and Trichloroquinonechlorimide.** By R. SCHMITT and M. ANDRESEN (*J. pr. Chem.* [2], **23**, 435—439).—By the action of bleaching powder solution on a hot solution of paramidophenol hydrochloride in concentrated hydrochloric acid, a mixture of tri- and tetra-chloroquinone is obtained, which by the further action of hydrochloric acid is converted into tetrachloroquinol.

When bleaching powder solution is added to paramidophenol hydrochloride suspended in concentrated hydrochloric acid in the cold, the hydrochlorides of di- and tri-chloramidophenol are formed, which by further addition of bleaching powder yield trichloroquinone. By passing chlorine into hydrochloric acid containing paramidophenol hydrochloride in suspension, trichloramidophenol hydrochloride is obtained, which when treated with bleaching powder solution yields trichloroquinonechlorimide,  $C_6H.Cl_3\overset{N}{O}>Cl$ . For an account of the

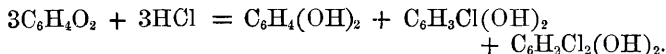
products of the action of this chlorimide on amines, see this vol., 400. P. P. B.

**Phlorone and Xyloquinone.** By E. CARSTANJEN (*J. pr. Chem.* [2], **23**, 421—435).—By oxidising creosote with sulphuric acid and manganese dioxide, Rommier and Bouilhon obtained two quinones, one melting at 60—62°, and the other at 125°; the former they styled phlorone, the latter metaphlorone. By crystallising from alcohol the product of oxidation of yellow carboic acid (b. p. 194—235°), viz., crude phlorone, the author obtained a substance melting at 123·5°, which proved to be xyloquinone. The alcoholic mother-liquors yield a mixture of quinone, from which, after conversion into the quinols and crystallisation from benzene, xyloquinol is obtained, and also toluquinol,  $C_7H_8O_2$  (m. p. 69°). Hence phlorone is a mixture of xylo- and tolu-quinones.

That this xyloquinone is a para-derivative is shown not only by its identity with that described by Nietzky (this Journal, **38**, 552), but also by its yielding paraxylene when distilled over zinc-dust. It is also formed by the oxidation of crude xyloidine, and may be obtained from xylene (b. p. 139—140°) by converting it first into a sulphonic acid, then into xylenol by fusion with potash, and finally oxidising the xylenol so obtained.

The author has prepared xyloquinol (m. p. 208°) described by Nietzky (*loc. cit.*). This compound when heated with concentrated hydrochloric acid, yields a substance melting at 148—150°, which on oxidation yields monochloro- (m. p. 48°) and dichloro-xyloquinone (m. p. 175°).

Dichloroxyloquinol may be separated from the product melting at 148—150°, by crystallising it from hot aqueous alcohol; the last mother-liquors yield a small quantity of the monochloroxyloquinol (m. p. 147°), which on oxidation yielded the quinone (m. p. 48°). This monochloro-derivative is converted into the dichloro-derivative by boiling with hydrochloric acid. Quinol when treated with hydrochloric acid, also yields a mono- and di-chlorohydroquinol, the formation of which may be explained as follows:—



Dibromoxyloquinol is obtained by the action of bromine on xyloquinone suspended in water. It is insoluble in water, sparingly soluble in cold alcohol, more easily in hot alcohol, from which it crystallises in golden shining leaflets (m. p. 184°). This compound is with difficulty converted into the corresponding quinol. P. P. B.

**Preparation of Phenyl-propyl-ketone.** By E. BURCKER (*Bull. Soc. Chim.* [2] **37**, 4—5).—Phenyl-propyl-ketone is readily obtained by the action of butyric chloride on an excess of benzene in presence of aluminium chloride. When evolution of hydrochloric acid ceases, the product is thrown into water in small quantities at a time, when the ketone remains dissolved in the excess of benzene.

C. H. B.

**Phorone from Glycerol.** By K. E. SCHULZE (*Ber.*, 15, 64—66).—A 3 per cent. solution of glycerol is sown with a fermenting extract of meadow hay, and left to ferment in well-stoppered flasks, at a temperature of 37—38°, ammonium and potassium phosphates and sulphates being used as food for the ferment. After ten weeks, the fermented liquid is distilled, and the distillate treated with potassium carbonate; the alcoholic layer is then separated, dried, and fractioned. In this way, from 3 kilos. of glycerol 32 grams of a fraction boiling at 218° (thermometer entirely in vapour), is obtained. This body yields on analysis numbers agreeing with the formula  $C_9H_{14}O$ , phorone; it is a colourless, oily liquid (sp. gr. at 15°, 0.9645) with a characteristic turpentine-like odour, and a burning taste. It forms with bromine an unstable addition-product, and with phosphorous pentachloride an equally unstable chloride. With concentrated sulphuric acid, it gives a dark red coloration, and with nitric acid (sp. gr. 1.4), in the cold a red colour, but on heating, a violent reaction takes place, and a solid greyish yellow nitro-body is produced.

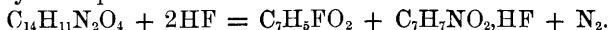
Phorone, along with other products, including acetone, is also obtained when a mixture of 5 parts of glycerol, 8 parts of lime, and 6 parts of zinc-dust are well rubbed together, strongly heated, and then burnt in a current of hydrogen. This phorone is a slightly yellow liquid (sp. gr. 0.9110; b. p. inconstant, 205—225°); it gives a scarlet coloration with concentrated sulphuric acid, and a liquid nitro-body with nitric acid.

The difference between these two phorones, the author thinks, is probably due to impurities.

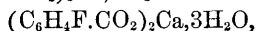
D. A. L.

**Researches on the Three Isomeric Fluobenzoic Acids, and on Fluotoluic and Fluoanisic Acid.** By E. PATERNÒ and V. OLIVERI (*Gazzetta*, 1882, 85—96).—I. FLUOBENZOIC ACIDS,  $C_6H_4F.COOH$ .

—1. *Parafluobenzoic acid* [ $F : COOH = 1 : 4$ ], was prepared by adding 12—15 g. paradiamidobenzoic acid (obtained by the usual series of processes from *p*-nitrotoluene) to 200 c.c. of highly concentrated hydrofluoric acid contained in a platinum capsule, gently heating the mixture, whereupon it becomes frothy from evolution of nitrogen, and stirring it continually with a rod of platinum or ebonite, till the reaction is complete. On then leaving it to cool, the greater part of the fluobenzoic acid is deposited, and may be purified by crystallisation from boiling water, with addition of a small quantity of animal charcoal. In solution there remains the hydrofluoride of *p*-amidobenzoic acid (m. p. 210—211°). The formation of these two acids is represented by the equation—



Parafluobenzoic acid prepared as above crystallises from boiling water in flat needles, having a nacreous lustre, resembling benzoic acid in aspect and odour, soluble in alcohol, ether, benzene, &c., melting at 180—181°, and volatilising without decomposition. Its *barium salt* crystallises from boiling water in ill-defined and not quite colourless laminæ, moderately soluble in hot, slightly in cold water, and having the composition  $(C_6H_4F.CO_2)_2Ba.4H_2O$ .—The *calcium salt*,



prepared in like manner, forms ill-defined scales, always having a yellow colour, very soluble in water, both hot and cold.

Parafluorobenzoic acid was first obtained in 1870, by Schmitt and Gehren (*J. pr. Chem.* [2], 7, 394), who however regarded it as the meta-derivative, inasmuch as they obtained it by the action of hydrofluoric acid on the diazo-acid prepared from ordinary amidobenzoic acid, which is known to be a meta-compound. It is probable, however, that the amidobenzoic which they used consisted, partly at least, of the para-modification, since, as will presently be seen, the true metafluorobenzoic acid melts at a much lower temperature than the acid obtained by them, which in fact melted at  $182^{\circ}$ , agreeing therein very nearly with the para-acid above described.

2. *Metafluorobenzoic acid* [1 : 3], was prepared in like manner from diazometamidobenzoic acid, and was deposited from the resulting solution on cooling, while the mother-liquors yielded the *hydrofluoride of metamidobenzoic acid* in needles melting at  $175^{\circ}$ . The metafluorobenzoic acid, purified by two crystallisations from boiling water, forms laminæ similar to those of benzoic acid, perfectly colourless, and melting at  $123-124^{\circ}$ . Its *barium* and *calcium salts* crystallise with 3 mol. water. The *silver salt* crystallises from boiling water in hard colourless anhydrous needles, altered by exposure to light. The *sodium salt* separates from boiling aqueous solution in arborescent groups of large white opaque scales, containing 1 mol.  $H_2O$ . The *methylic ether*,  $C_6H_4F.COOMe$ , prepared by the action of methyl iodide on the silver salt, is a colourless, transparent, strongly refracting liquid, having a fragrant odour like that of benzoic ethers in general, and boiling at  $192-194^{\circ}$ .

3. *Orthofluorobenzoic acid* [1 : 2] is prepared by the action of hydrofluoric acid on diazo-orthamidobenzoic or diazo-amidoanthranilic acid,\* the heating being, however, continued for a longer time than in the preceding cases, because the action is slower, and separates on cooling in crystals, which may be purified by recrystallisation from boiling water. It then forms nearly colourless slender needles, more soluble in boiling water than its isomerides, easily soluble in alcohol and ether, and melting at  $117-118^{\circ}$ . Its *barium salt* crystallises in light, slightly yellow laminæ, containing  $2H_2O$ , and very soluble in water. The *calcium salt*, also containing  $2H_2O$ , resembles it in every respect, excepting that it may be obtained quite colourless.

The *hydrofluoride of orthamidobenzoic acid*, obtained from the mother-liquors of the *o*-fluorobenzoic acid, forms silky, very soluble needles, melting with decomposition at about  $200^{\circ}$ .

II. FLUOTOLUIC ACID,  $CH_3.C_6H_4F.COOH$ , is prepared similarly to the preceding acids, by heating diazo-paramidotoluic acid with concentrated hydrofluoric acid, but does not separate from the resulting

\* This acid is prepared by dissolving anthranilic acid in the smallest possible quantity of ethyl nitrite, and adding an excess of anhydrous ether saturated with nitrous gas, and separates in a mass of crystals, colourless at first, but gradually turning yellowish; it decomposes at  $80^{\circ}$  with violent explosion. The use of ether in its preparation (instead of alcohol, which is used in preparing the corresponding meta- and para-acids) is necessitated by the circumstance that it is easily soluble in alcohol.

solution on cooling; on neutralising the liquid with soda, however, then concentrating, and adding hydrochloric acid, a flocculent precipitate is obtained, which, when dried and purified by repeated crystallisation from a mixture of alcohol and water, in presence of animal charcoal, yields white scales, melting at  $160-161^{\circ}$ , and agreeing in composition with the formula above given.

III. FLUOANISIC ACID,  $\text{MeO.C}_6\text{H}_3\text{F.COOH}$ , prepared in like manner from diazo-amido-anisic acid, separates as a flocculent substance, which, when washed with a little water and crystallised from aqueous alcohol, in presence of animal charcoal, forms slender colourless needles, melting at  $204^{\circ}$ .

The experiments above described show—in opposition to the results obtained by Schmitt and Gehren—that the fluobenzoic acids melt at lower temperatures than the corresponding chlorobenzoic acids, so that, in this class of organic compounds, fluorine takes its place in the series of halogen-elements before chlorine, in accordance with its lower atomic weight. Moreover, the difference between the melting points of ortho- and meta-fluobenzoic acids ( $6^{\circ}$ ) is small in comparison with that which exists between the melting points of the meta- and para-compounds ( $57^{\circ}$ ), in which respect the fluobenzoic acids resemble the other halogen-derivatives of benzoic acid; thus in the chlorobenzoic acids the difference of melting point between the *o*- and *m*-acid is only  $16^{\circ}$ , whereas between the *m*- and *p*-acids it is  $34^{\circ}$ ; in the corresponding brominated acids these differences are respectively  $13^{\circ}$  and  $93^{\circ}$ , and in the iodated acids,  $28^{\circ}$  and  $80^{\circ}$ . In the present state of our knowledge, however, it would be premature to extend this relation to other classes of halogenated organic compounds; and in fact the only other example that could at present be cited, namely, the fluobenzene obtained by Schmitt and Gehren, tends to an exactly opposite conclusion, inasmuch as this compound is solid at ordinary temperatures, melts at  $40^{\circ}$ , and boils at  $180-183^{\circ}$ , whereas monochloro-, monobromo-, and mono-iodobenzene are liquids, boiling respectively at  $132^{\circ}$ ,  $155^{\circ}$ , and  $185^{\circ}$ . The authors hope soon to continue their experiments on fluorated organic compounds, with the view of throwing further light on these relations.

H. W.

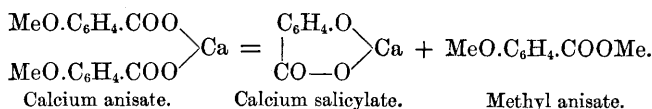
**Behaviour of the Isomeric Monobromocinnamic Acids with Concentrated Sulphuric Acid.** By R. LEUCKART (*Ber.*, 15, 16—21).—Glaser (*Annalen*, 143, 325, *et seq.*), by treating dibromocinnamic acid with alcoholic potash, obtained two isomeric monobromophenylacrylic acids, which he called  $\alpha$ - $\beta$ -monobromocinnamic acids.

When treated with cold concentrated sulphuric acid, the  $\alpha$ -acid dissolves readily, but undergoes scarcely any change, very small quantities of acetophenone being the only product. The  $\beta$ -acid, on the other hand, under similar circumstances, is readily altered; it dissolves to a yellow solution, which gradually passes through different shades to brown. The product is poured into water, by which it is precipitated in flocks. The precipitate is washed, and treated with dilute soda-solution; the part soluble in soda contains the body  $\text{C}_{19}\text{H}_{12}\text{O}$ , which crystallises from a mixture of nitrobenzene and glacial acetic acid in yellow

needles (m. p. above  $260^{\circ}$ ), soluble in most of the ordinary solvents. The neutral ammoniacal solution gives yellow insoluble precipitates with metallic chlorides; the acid is easily re-obtained from these salts. The part insoluble in soda was treated successively with glacial acetic acid, absolute alcohol, phenol, and dilute soda, then washed with water, alcohol, and ether, until the phenol odour had gone. The residue when heated to  $250^{\circ}$ , gave off phenol, and the residual substance soon decomposed, giving off a pungent vapour, only a very small quantity subliming without decomposition. The phenol compound is very sparingly soluble in most solvents; it is however decomposed by prolonged boiling with acetic anhydride: on cooling, iridescent leaflets separate out; they are free from phenol, and contain bromine, but are difficult to purify. The product from the action of butyric anhydride crystallises in large leaflets with mother-of-pearl lustre, soluble in boiling phenol, nitrobenzene, aniline, and high boiling coal-tar oils, with all of which it forms crystalline compounds. On analysis this product yields numbers for the formula  $C_{17}H_{11}Br_2O_2$ , or  $C_{17}H_{12}Br_2O_2$ ; it melts above  $340^{\circ}$ , dissolves with change in concentrated sulphuric acid, and on being boiled with alcoholic potash for some time, decomposes with a characteristic violet coloration. It is very stable towards oxidising agents. By treating the phenol compound suspended in glacial acetic acid with zinc-dust, a body,  $C_{17}H_{14}O_2$ , or  $C_{17}H_{13}O_2$ , is formed, sparingly soluble in water, easily in alcohol, from which it separates in beautiful crystals (m. p.  $127^{\circ}$ ). It dissolves in concentrated sulphuric acid, with rose-red colour, and gives a violet coloration when heated with alkalis. This body is not the only product of the above reduction. The paper concludes with some theoretical considerations.

D. A. L.

**Decomposition of the Calcium Salts of the three Hydroxybenzoic Acids and of Anisic Acid by Dry Distillation.** By G. GOLDSCHMIEDT and J. HERZIG (*Monatsh. Chem.*, 126—135).—1. *Calcium anisate* yields by dry distillation an oily product consisting of anisole, phenol, and methyl anisate, and a residue containing the calcium salts of salicylic and  $\alpha$ -hydroxyisophthalic acids, together with calcium carbonate and greasy products. The formation of the methyl anisate appears to take place according to the equation:—



The conversion of parahydroxybenzoic acid into salicylic acid by the action of heat on its salts, and the formation of dicarboxylic acids by heating these same salts in an atmosphere of carbonic anhydride, have been established by the researches of Kupferberg (this Journal, 29, 926), Ost (*ibid.*, 29, 252), and van d. Velden (*ibid.*, 32, 337). The formation of anisole and phenol by the action of heat on anisates and hydroxybenzoates respectively are well known facts.

2. The calcium salts of parahydroxybenzoic and salicylic acid yield by dry distillation products nearly identical with those obtained by



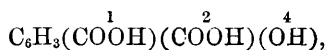
the three chemists just mentioned from the alkali-salts of the same acid; but the decomposition of calcium metahydroxybenzoate takes place in a different way.

When dehydrated *calcium parahydroxybenzoate* is subjected to dry distillation, phenol passes over, together with a small quantity of a substance insoluble in alkalis, smelling like diphenylene oxide, crystallising from alcohol in long, mostly curved, white needles, and melting at 99°. The quantity of this substance obtained was too small for complete examination, but it may probably be regarded as the diphenylene oxide of the para-series. The residue of the distillation of the parahydroxybenzoate was found to consist of the same substances as those obtained from the anisate, viz., basic salicylate,  $\alpha$ -hydroxyisophthalate, and carbonate of calcium, together with greasy products.

That calcium *salicylate* decomposes at high temperatures in the same manner as the sodium salt has already been shown by Ost, and the authors of the present paper have likewise found in the residue, which was nearly white, nothing but basic salicylate of calcium. The phenol in the distillate when dissolved in alkali, left a small quantity of diphenylene oxide, crystallising from alcohol in laminæ, melting at 80—81°, and forming with picric acid a yellow compound melting at 94° (cf. M. v. Schmidt, *Monatsh.*, **2**, 15; this Journal, 1881, Abstr., 824). The formation of diphenylene oxide by the distillation of calcium salicylate, and its non-production in like manner from the para- or meta-hydroxybenzoate (*infra*) points to the conclusion that it is an ortho-compound, and is produced in this case, not from previously formed phenol, but from the residues of calcium salicylate.

*Calcium metahydroxybenzoate* yields a greenish distillate, the last portions of which solidify. This distillate dissolves in potash-ley, forming a slightly turbid red solution; and on agitating this with ether, the turbidity disappears, the ether acquiring a yellow-green fluorescence, and leaving on evaporation a very small quantity of a greasy substance having a faint odour of diphenylene oxide. The alkaline solution when acidulated deposits phenol, together with metahydroxybenzoic acid.

The residue contained—together with unaltered metahydroxybenzoic acid—salicylic acid and acids precipitable by lead acetate; and on decomposing the lead precipitate with hydrogen sulphide, agitating the filtrate with ether, and recrystallising the residue from water, with the aid of animal charcoal, the crystals which separated melted at about 180°, and gave no colour-reaction with ferric chloride, whereas the mother-liquors and the second crop of crystals melting at a temperature 100° higher, exhibited the red iron reaction. Hence it appears that in the distillation of calcium metahydroxybenzoate, salicylic and  $\alpha$ -hydroxyisophthalic acid are formed—as from parahydroxybenzoic acid—and in addition, most probably also, hydroxy-orthophthalic acid, which, according to Baeyer (*Ber.*, **10**, 1079) and Schall (*ibid.*, **12**, 816), melts at 181°, is precipitable by lead acetate, and does not give any iron reaction. This acid,

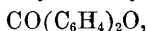


may be formed from metahydroxybenzoic acid without change of orientation.

As already observed, the behaviour of calcium metahydroxybenzoic acid when heated is totally different from that of the alkali-salts of the same acids, which, as shown by Kupferberg, yield neither polybasic acids, nor isomeric hydroxybenzoic acids, nor phenol.

H. W.

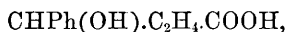
**Action of Phosphorus Oxychloride on Neutral and Basic Sodium and Potassium Salicylates.** By R. RICHTER (*J. pr. Chem.* [2], 23, 349—351).—By the action of phosphorus oxychloride on basic sodium or potassium salicylate, oxydiphenyl ketone,



is obtained, identical with that described by Merz and Weith (this Journal, Abstr., 1881, 264). This compound is also produced by distilling phenyl phosphate with the above salicylates, also by the dry distillation of sodium chlorosalicylate. Hydriodic acid converts it at  $160^\circ$  into methylene diphenyl oxide. By sodium amalgam, it is converted into a compound,  $\text{C}_{26}\text{H}_{18}\text{O}_3$  (m. p.  $199^\circ$ ). An isomeride of this ketone is obtained by acting on neutral sodium salicylate with phosphorus oxychloride. This ketone is soluble in alkalis, is but slightly acted on by hydriodic acid, and melts at  $91^\circ$ . Heated with caustic lime, it yields diphenyl oxide and diphenyl ketone. Both ketones form bromo-substitution-compounds, sulphonic acids, and nitro-compounds; the second ketone is decomposed by fuming nitric acid, yielding nitro-derivatives and carbonic anhydride.

P. P. B.

**Benzhydroxylpropionic Acid.** By E. BURCKER (*Bull. Soc. Chim.* [2], 37, 5—6).—*Benzhydroxylpropionic acid*,

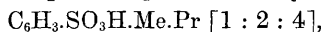


is obtained by the action of nascent hydrogen (from sodium amalgam, or zinc and HCl in alcoholic solution) on benzoylpropionic acid. It forms white orthorhombic needles, m. p.  $30\text{--}31^\circ$ , b. p.  $235^\circ$ , readily soluble in alcohol, ether, chloroform, and boiling water, but insoluble in cold water. By oxidation with chromic mixture, it is reconverted into benzoylpropionic acid. Benzhydroxylpropionic acid is the higher homologue of phenyl-glycollic and phenyl-lactic acids. It forms salts which crystallise with difficulty. On adding silver nitrate to a solution of the barium salt, the silver salt is obtained as a white precipitate, rapidly decomposed by light.

C. H. B.

**Displacement of the Sulpho-group by Bromine.** By W. KÄLBE (*Ber.*, 15, 39—42).—This paper is in support of the view expressed by the author in a previous communication (this vol., 301). He has further investigated the bromocymene produced by the action of bromine on the aqueous solution of  $\alpha$ -metaisocymenesulphonic acid in the cold (*ibid.*, 300). He calls this  $\alpha$ -bromometaisocymene; it is a colourless highly refractive liquid (b. p.  $233\text{--}235^\circ$ ) with a rose-like odour. Heated with ordinary concentrated sulphuric acid, it dissolves and carbonises, hydrobromic acid being at the same time given off. Fuming sulphuric acid dissolves it at the ordinary temperature,

forming a bromocymenesulphonic acid, which crystallises from concentrated hydrochloric acid in long fine needles. This bromocymene is likewise dissolved by fuming nitric acid, from which solution water separates an oil, which crystallises on standing, and after purification and recrystallisation from boiling light petroleum, forms long thick reddish needles (m. p.  $121^{\circ}$ ); this is *nitrobromocymene*. By boiling  $\alpha$ -bromocymene with dilute nitric acid, it is converted into an acid which crystallises from alcohol in warty groups of thick needles (m. p.  $210\cdot5^{\circ}$ ), identical with O. Jacobsen's bromometatoluic acid (this vol., 185) Br : Me : COOH = [1 : 2 : 4]. Therefore the formulæ for the different bodies from cymene can be thus represented: the bromocymene,  $C_6H_3.Br.Me.Pr$  [1 : 2 : 4], and the sulphonic acid,

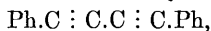


and the phenol from the sulphonic acid,  $C_6H_3.OH.Me.Pr$ . [1 : 2 : 4].

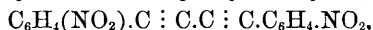
By the action of concentrated hydrochloric acid on the monobrom- $\alpha$ -metaisocymenesulphonic acid already described (*loc. cit.*, 300), another bromocymene is obtained: this is called  *$\beta$ -bromometaisocymene*; it is a colourless strongly refractive liquid (b. p.  $224\text{--}225^{\circ}$ ), with an odour of bromotoluene. It dissolves in fuming nitric acid forming *dinitrobromocymene*, which crystallises from light petroleum in nodular aggregations of short thick needles (m. p.  $55^{\circ}$ ).  *$\beta$ -bromocymene* is not so easily attacked by dilute nitric acid as the  $\alpha$ -bromocymene; it is, however, ultimately converted into an acid (m. p.  $155^{\circ}$ ).

D. A. L.

**Compounds of the Indigo-group.** By A. BAEYER (*Ber.*, 15, 50—56). In a previous communication (this vol., 198—199) it was shown that the formation of indigo-blue probably depends on the production and ultimate oxidation of an intermediate body—indoxyl. This change into the colouring-matter is most likely accompanied by a carbon condensation effected between the carbon-atoms farthest away from the benzene-group. If then this is so, the hydrocarbon from which indigo is derived must be Glaser's diacetylenylphenyl,—

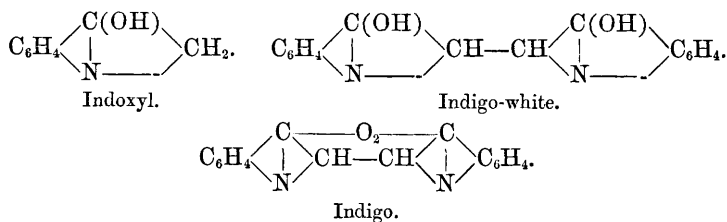


(*Annalen*, 154, 159). To prove this, the author has prepared the orthonitro-derivative of this hydrocarbon in the following way:—On boiling orthonitrophenylpropionic acid with water, the presence of mineral acids being avoided, orthonitrophenylacetylene is formed, and passes over with the steam. It is converted into the copper-compound by dissolving in much alcohol and precipitating with ammoniacal cuprous chloride. One part of this copper compound (moist) is left in a solution of potassium ferricyanide (2.25 parts), and potassium hydroxide (0.38 part), in water (9 parts), until the red colour has disappeared, which takes about 24 hours; the precipitate is then washed and extracted with chloroform. The required nitro-derivative crystallises out in golden-yellow needles from the chloroform. The author calls this body *orthodinitrodiphenyldiacetylene*,—

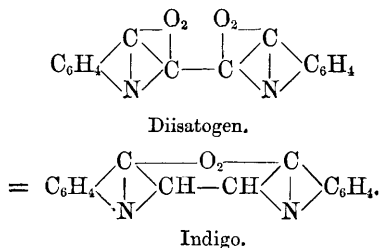


it is insoluble in cold alcohol and ether, only very sparingly soluble in hot alcohol, but soluble in chloroform and nitrobenzene. It melts with

decomposition at  $212^{\circ}$ . It is not easily reduced. Ferrous sulphate in the presence of concentrated sulphuric acid reduces it to indoin. This body, like ethyl orthonitrophenylpropionate, is converted into its isomeric isatogen derivative—diastogen—by the action of concentrated sulphuric acid. When finely powdered dinitrodiphenyldiacetylene is mixed with concentrated sulphuric acid, fuming sulphuric acid then gradually added until all is dissolved, and the dark cherry-red liquid filtered through glass-wool and allowed to drop into alcohol, *diisatogen* separates out in red needles. This body, like indigo, is insoluble in alcohol and ether, somewhat soluble in chloroform, but more readily in hot nitrobenzene, from which it crystallises in red needles. It is of special interest because of all artificial substances it is the nearest allied to indigo, and the most easily converted into it. It is converted directly into *indigo* free from indirubin, and without passing through the intermediate stages of either indigo-white or indoxyl, by reducing agents such as ammonium and alkaline sulphides, zinc, and ammonia, or potash, or acetic acid, &c. By concentrated sulphuric acid and ferrous sulphate, it is changed to indoin. Tin and hydrochloric acid yield a yellow amorphous substance, similar to that produced by the same reagents with indigo. The formation of indigo from indoxyl may be thus represented:—



As the nature of the isatogen-group is not yet definitely established, the formation of indigo from diisatogen cannot be represented with the same certainty, but may be provisionally explained thus:—



To ascertain the nature of the isatogen-group, experiments were made on its derivatives. By reduction, ethyl isatogenate is converted into ethyl indoxylate, and diisatogen into indigo. Both substances give indoin with concentrated sulphuric acid and ferrous sulphate. On treating the finely powdered ethyl isatogenate with barium hydroxide, and adding an acid as soon as barium carbonate separates out, then extracting with ether, a colourless oily acid is obtained, which is soluble

in water, and like phenylglyoxylic acid gives a red colour with benzene and concentrated sulphuric acid; it is therefore probably a derivative of this acid, *azophenylglyoxylic acid*. By continuing the action of barium hydroxide solution, orthoazobenzoic acid (Griess, *Ber.*, **10**, 1869) is formed. With sodium carbonate, isatin is produced, as well as azobenzoic acid. Diisatogen at first dissolves in baryta-water, but in a very short time indigo is precipitated, and azobenzoic acid remains in solution; with sodium carbonate diisatogen also forms azobenzoic acid. Ethyl isatogenate forms with potassium or ammonium hydrogen sulphite, a compound which is converted into indoxyl, evidently passing through the stage of isatogen sulphite. Orthonitrophenylpropionic acid likewise gives rise to isatogensulphurous acid when boiled with ammonium-hydrogen sulphite. *Isatogensulphurous acid* can be isolated by precipitating the sulphurous acid with barium acetate, the barium with ammonium carbonate, acidifying with acetic acid, and precipitating with lead acetate, &c. It forms a yellow syrup, is converted by concentrated sulphuric acid into indoin, and by ammonia and zinc-dust into indoxyl, which quickly oxidises to indigo in the air. Ammonium hydrogen sulphite does not convert dinitrodiphenyldiacetylene into an isatogen derivative. Diisatogen combines directly with the sulphite, and on boiling dissolves to a yellow solution, which after removal of the sulphurous acid with barium acetate behaves similarly to a solution of isatogensulphurous acid, with the exception that with zinc-dust and ammonia it forms indigo direct and not indoxyl. The author could not prepare free isatogen from its sulphite compound, which is remarkable because the corresponding compound of its isomeride, isatin, decomposes spontaneously.

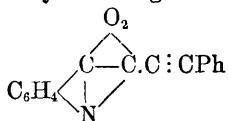
D. A. L.

**Preparation of Triphenylmethane.** By C. FRIEDEL and J. M. CRAFTS (*Bull. Soc. Chim.* [2], **37**, 6—11).—The method recently described by Schwarz for the preparation of triphenylmethane by the action of aluminium chloride on chloroform in presence of benzene, was described by the authors in 1877. Later E. and O. Fischer found that diphenylmethane is produced in considerable quantity, and attribute its formation to reduction of an intermediate product,  $\text{CHCl}(\text{C}_6\text{H}_5)_2$ , by the aluminium chloride, a supposition which agrees with the authors' theory of the intermediate formation of the compound  $\text{Al}_2\text{Cl}_6\text{C}_6\text{H}_5$ . The best yield of triphenylmethane was obtained by mixing 1,000 grams benzene, 200 grams chloroform, and 200 grams aluminium chloride, the latter being added in four or five portions, and the liquid finally heated to the boiling point of benzene for two hours. Only 130 grams hydrochloric acid were evolved, instead of 183.4, as required by the equation  $\text{CHCl}_3 + 3\text{C}_6\text{H}_6 = \text{CH}(\text{C}_6\text{H}_5)_3 + 3\text{HCl}$ . Fischer's theory of the formation of diphenylmethane requires the evolution of the whole of the hydrochloric acid. That portion of the distillate boiling above  $150^\circ$  weighed 280 grams. On heating to  $200^\circ$  it gave off hydrochloric acid and a small quantity of water, and yielded on fractionation 40 grams diphenylmethane, 150 grams triphenylmethane, 50 grams carbonaceous residue, and other substances of higher boiling point than triphenylmethane. The diphenylmethane

does not appear to be formed in presence of the aluminium chloride, but when the crude product is heated to  $200^{\circ}$ , probably by the mutual reaction of the chloride  $\text{CHCl}(\text{C}_6\text{H}_5)_2$  and the triphenylmethane, the latter possibly being converted into  $\text{C}_2(\text{C}_2\text{H}_5)_6$ . Prolonged boiling with zinc and hydrochloric acid in alcoholic solution, or treatment with potash, fails to remove chlorine from the crude product. When triphenylmethane is heated for 10 minutes at  $120^{\circ}$  with one-third its weight of aluminium chloride, it is almost entirely decomposed, with production of benzene and a hydrocarbon which resembles asphalt, but entirely decomposes on heating, yielding benzene. It follows that in preparing triphenylmethane prolonged heating should be avoided. When 1 part triphenylmethane is heated with 7.5 parts benzene, and 1 part aluminium chloride, for 10 hours at a temperature below the boiling point of benzene, it yields more than one-third its weight of diphenylmethane, but cannot be entirely decomposed. Toluene is not formed in the process of preparing triphenylmethane. C. H. B.

### Synthesis by means of Phenylacetylene and its Derivatives.

By A. BAEYER and L. LANDSBERG (*Ber.*, **15**, 57—61).—*Diphenyldiacetylene* can be prepared by mixing a quantity of phenylacetylene-copper, equivalent to 1 mol. of the acetylene, with a cold saturated solution of 1 mol. of potassium ferricyanide mixed with 1 mol. potash, and leaving the mixture until the flocks of the original copper compound are changed into greenish-brown granular precipitate (about 24 hours). The precipitate is washed, dried, and extracted with alcohol. This method is adopted throughout this paper for the preparation of acetylene derivatives, the solvent for extraction being varied. *Orthomononitrodiphenyldiacetylene* is prepared by treating the copper compound of phenylacetylene and its orthonitro-derivative by the above method; or by dissolving the two substances together in alcohol and treating them with ammoniacal cuprous chloride. The copper precipitate is extracted with chloroform, the chloroform distilled off, and the residue crystallised from alcohol. The first crop consists of a small quantity of the dinitro-derivative, the second is the mononitro-body, and the mother-liquor retains the non-nitrated diacetylene. *Orthomononitrodiphenyldiacetylene*,  $\text{NO}_2.\text{C}_6\text{H}_4.\text{C}:\text{C}:\text{C}:\text{C}.\text{C}_6\text{H}_5$ , crystallises from alcohol in yellow leaflets (which soften at  $145^{\circ}$ , and melt at  $154\text{--}155^{\circ}$ ). It is moderately soluble in alcohol and ether, and very easily in chloroform. The authors consider this body of special interest, because the group  $\begin{array}{c} \text{—C:C—} \\ \text{—NO}_2 \end{array}$ , which is so important in the formation of indigo, is present in a form of combination differing from the form found in all bodies previously described. Concentrated sulphuric acid dissolves it with a brown colour, evidently converting it into the isomeric phenylacetyleneisatogen—



This could not be obtained pure; on pouring into alcohol nothing sepa-

rated; but with water an amorphous red mass is formed, soluble in chloroform. Reduction experiments yielded no noteworthy results. Ammonium sulphide converts it into a brick-red substance, which could not be crystallised. Ferrous sulphate and sulphuric acid do not act on it. From this it is apparent that when the carbethoxyl group in an isotogenic ethereal salt is replaced by a hydrocarbon, it cannot be converted into an indigo-body.

*Orthamidophenylacetylene*.—Finely powdered nitrophenylacetylene is shaken up with ammonia and zinc-dust; when the action is finished, the mass is distilled with steam, the distillate extracted with ether, and the extract shaken with hydrochloric acid. The base is separated from the latter by adding soda. It is a pale yellow oil with an odour something like that of naphthalene, or when diluted, like that of the indigo-vat. It becomes brown and viscid on exposure to the air. A pine chip moistened with alcohol and hydrochloric acid is coloured yellow when dipped into amidophenylacetylene. An alcoholic solution of this base is precipitated pale yellow by ammoniacal silver solution, and yellow by ammoniacal cuprous chloride. The silver derivative decomposes while drying, and detonates on heating; the copper derivative is more stable. The *hydrochloride*,  $C_8H_8NCl$ , is an unstable yellow crystalline mass, easily soluble in water. The *acetate*,  $C_{10}H_9NO$ , made by mixing the base with acetic anhydride, crystallises from water in colourless needles (m. p.  $75^\circ$ ). As the diamido-derivatives of diphenyl-diacetylene are easily decomposable, acetyl-compounds are used.

*Orthodiamidodiphenyldiacetylene*,  $NH_2.C_6H_4.C:C:C.C_6H_4.NH_2$ .—The acetate of this body is prepared by treating the copper-compound of acetylamidophenylacetylene by the potassium ferricyanide method. The copper precipitate is extracted with chloroform, and the extract crystallised from alcohol, boiled with equal parts of water, sulphuric acid and alcohol, until all is dissolved. This is now poured into water, filtered if necessary, and the base precipitated by ammonia. It crystallises from dilute alcohol in long yellowish prisms (m. p.  $128^\circ$ ), insoluble in water, easily soluble in alcohol, ether, and acids. The *hydrochloride*,  $C_{16}H_{12}N_2.2HCl$ , obtained in definite colourless crystals, by evaporating its solution in a vacuum, is easily soluble in water. The *diacetate*,  $C_{16}H_{10}N_2.2AcO$ , forms long, colourless, very brilliant needles (m. p.  $231^\circ$ ), which turn rose-red on exposure to light.

D. A. L.

**Conversion of Phenols into Diphenols by Oxidation.** By A. P. DIANIN (*Journ. Russ. Chem. Soc.*, 1882, 130—152).—In the year 1877 the author published his researches on the oxidation of isomeric naphthols by ferric chloride. The results of his further researches have been partly published since, and are completely described in the present extended memoir.

*$\beta$ -Oxydinaphthylene*,  $C_{20}H_{12}O$ , is obtained on heating  $\beta$ -dinaphthol, after drying it at  $150^\circ$  with phosphorus pentoxide. It has a pale yellow colour, and exhibits a slight green fluorescence, is soluble in ether, benzene, boiling alcohol, and acetic acid, but colourless when pure. Its prismatic crystals melt at  $154^\circ$ . Its composition is analogous to that

of ethylene oxide. It combines with picric acid. *α-Oxydinaphthylene* is obtained in a similar way.

*Isomeric dithymols* were obtained on oxidising *α*- or *β*-thymol with ferric salts (either the chloride after neutralising it by marble or ferric alum), according to the equation:—



*α-Dithymol*, obtained from *α*-thymol, forms white prismatic or tabular crystals (m. p.  $165.5^\circ$ ), combining with alkalis to yellow solutions. It contains 1 mol. of water of crystallisation,  $C_{20}H_{26}O_2 + H_2O$ . On heating it with benzoic chloride, *α-dibenzoyl-dithymol*,  $C_{20}H_{24}Bz_2O_2$ , is obtained; it forms microscopic scales (m. p.  $215^\circ$ ), insoluble in water. With potassium hydroxide it splits up into benzoic acid and dithymol. The behaviour of *α*-cymol (carvacrol) on oxidation, is similar, but the products have not yet been completely investigated. The same is the case with ordinary phenol and meta-cresol. The author concludes his extended paper with theoretical remarks on the condensation of aromatic bodies, and points out that the condensation of phenols takes place more easily than that of other aromatic compounds, such as hydrocarbons, the last-named requiring the use of powerful reagents, high temperatures, &c. B. B.

**Naphthalene-tetrasulphonic Acid.** By C. SENHOFER (*Monatsh. Chem.*, **3**, 111—117).—By the action of a mixture of strong sulphuric acid and phosphoric anhydride on naphthalene, the author in 1875 obtained a naphthalene-tetrasulphonic acid, from the properties of which he was unable to decide whether it consisted of a single acid or of a mixture of two isomeric acids. On continuing his experiments, he finds that, on neutralising the crude acid obtained as above with cupric carbonate, dissolving the resulting cupric salt in hot water, and leaving the solution to cool very slowly, massive blue prisms separate out, while the mother-liquor exhibits a fine green colour, and, when slowly concentrated, deposits more of the blue crystals, which may be purified by recrystallisation. By still further concentration, mixtures of blue and green crystals are obtained, from which the former may be separated in the pure state so long as they predominate in the mixture; but the green crystals cannot be obtained free from the blue. Similar phenomena are exhibited by the barium and potassium salts prepared from the crude acid by neutralisation, each yielding a mixture of two salts, one of which, analogous to the blue copper salt, can be obtained pure, whereas the other cannot be completely separated from the former. The following descriptions apply to the salts corresponding with the blue copper salt:—

The *barium salt*, obtained by saturating the crude acid with barium carbonate, and leaving the solution to evaporate at ordinary temperatures, or at most at  $30$ — $35^\circ$ , separates in thick obliquely truncated prisms, having a yellow to brown colour; colourless crystals may, however, be obtained by boiling the pure acid, separated by hydrogen sulphide from the lead or copper salt, with baryta-water. The salt, dried at  $200^\circ$ , has the composition  $C_{10}H_4S_4O_{12}Ba$ . The crystals contain 7, 10, 13, or 15 mols. of water, according to the temperature at which



they are formed. Most of them effloresce quickly and completely on exposure to the air; others partially, and some not at all. The air-dry crystals dissolve only partially in hot water, the undissolved portions being opaque, and much less soluble than the original crystals. The aqueous solution is not precipitated by lead acetate, either normal or basic, and gives no colour reaction with ferric chloride. The *lead salt*, prepared by neutralisation, separates from the concentrated solution as a very soluble indistinctly crystalline mass, having the composition  $C_{10}H_4S_4O_{12}Pb + 6H_2O$ , and becoming anhydrous at  $150^\circ$ . The *copper salt*, obtained by neutralisation, separates after some time in thick well-defined blue prisms, having the composition  $C_{10}H_4S_4O_{12}Cu_2 + 12H_2O$ , and giving off 9 mols. water at  $150^\circ$ . The *silver salt* is easily soluble in water, and separates therefrom, in a vacuum, in slender needles, which contain  $C_{10}H_4S_4O_{12}Ag_4 + 2\frac{1}{2}H_2O$ , and do not give off their water at  $100^\circ$ ; they are but slightly altered by exposure to direct sunlight. The *potassium salt*,  $C_{10}H_4S_4O_{12}K_4 + 2H_2O$ , crystallises in tufts of slender needles, which do not give off their water at  $100^\circ$ . The *sodium salt*,  $C_{10}H_4S_4O_{12}Na_2 + 10H_2O$  (air-dried), forms well-defined four-sided prisms, which effloresce quickly in the air, and give off 8 mols. water at  $100^\circ$ .

The *free acid*, obtained by decomposing the copper salt with hydrogen sulphide, separates by evaporation in a vacuum over calcium chloride, in thick prisms, very easily soluble in water, having, when dried at  $100^\circ$ , the composition  $C_{10}H_4S_4O_{12} + 4H_2O$ , and giving off  $2\frac{1}{2}H_2O$  at  $150^\circ$ . It is insoluble in ether, and only slightly soluble in cold alcohol, does not decompose at  $170^\circ$ , but when more strongly heated, gives off gas, and leaves a residue containing sulphuric acid.

H. W.

**Cyanic Ether of Borneol.** By A. HALLER (*Compt. rend.*, **93**, 1511—1514).—A solution of sodium camphor and sodium borneol in toluene, prepared by Baubigny's method, is saturated with dry cyanogen, washed with water to remove sodium cyanide, and then treated with soda to extract the cyano-camphor. The toluene and the greater part of the unaltered camphor are distilled off at a temperature below  $150^\circ$ , and the residue extracted with boiling water, which, on cooling, deposits silky needles; these may be purified by crystallisation from alcohol. The same compound is obtained by the action of cyanogen on a solution of sodium borneol alone in toluene. It has the composition  $C_{11}H_{19}NO_2$ , which corresponds either with cyanoborneol plus 1 mol.  $H_2O$ , or with a compound of borneol with cyanic acid. The crystals belong to the monoclinic system, and show two kinds of hemihedrisism, some faces occurring only on angles to the left; others only on angles to the right. The compound is insoluble in cold, and but slightly soluble in hot water, readily in ether, alcohol, chloroform, and benzene. It melts at  $115^\circ$ , and sublimes partially at  $100^\circ$ . The alcoholic solution rotates a ray of polarised light to the right, but the rotatory power varies considerably with the method of preparation of the compound. Montgolfier has shown that the borneol obtained by Baubigny's method is a mixture of dextro-borneol and unstable lævo-borneol: hence it is probable that the product obtained by the author

is a mixture of dextro-cyanoborneol, with unstable lævo-cyanoborneol. When fused with potash, it yields camphol, potassium carbonate, and ammonia; and if its alcoholic solution is heated with the theoretical quantity of potash, potassium cyanate and borneol are formed. Heated in dry hydrochloric acid gas, it yields ammonium chloride and the compound  $C_{10}H_{17}Cl$ ; heated alone to  $200-210^{\circ}$ , it splits up into borneol and cyanuric acid. It would appear, therefore, that the compound is a cyanic ether of borneol, *i.e.*, a compound of borneol with cyanic acid.

The author proposes to prepare cyanic ethers by the action of cyanogen on the alkaline alcoholates and phenates. C. H. B.

**Contributions to the Chemistry of the Rhizome of Zinziber Officinalis.** By J. C. THRESH (*Pharm. J. Trans.* [3], 12, 721—722).—It has been shown that besides a volatile oil, the ethereal extract of ginger contains seven different constituents, of these the following have been studied:—

The natural resin is represented by the formula  $C_{16}H_{24}O_3$ . On fusion with potash, which acts on it only with difficulty, a crystalline acid is obtained, which gives a green coloration with ferric chloride, changing to red on addition of soda. It is probably 3:4 dihydroxybenzoic acid.

*Resin  $\alpha$ .*—The portion of the ethereal extract not volatilised in steam and soluble in alcohol contains two resins,  $\alpha$  and  $\beta$ , besides the active principle, and a fourth substance, probably a terpene polymeride. The resins are only incompletely separated by precipitation with basic lead acetate, the precipitate being sparingly soluble in alcohol; whilst excess of lead acetate carries down some of the active principle. The precipitate is decomposed with sulphuric acid, excess of acid removed, and the solution fractionally precipitated. A brown lead salt, consisting chiefly of the  $\alpha$ -resin, is first precipitated, which is purified by repeating the above process, then boiling with benzene until nothing further is taken up by that solvent, and finally drying at  $100-200^{\circ}$ . The resin is very hard and brittle, of a jet-black colour, and having the composition  $C_{46}H_{54}O_{10}$ . All attempts to crystallise it have failed. It forms two lead salts, a neutral salt,  $Pb.C_{46}H_{52}O_{10}$ , and a basic salt,  $Pb_2O_3.C_{46}H_{52}O_{10}$ . By fusing it with potash an acid is obtained similar to that yielded by the natural resin.

*Resin  $\beta$ .*—By repeated fractional precipitation, this resin is obtained free from volatile oil, and probably from the  $\alpha$ -resin. It is soft, and of a red-brown colour. Its composition is represented either by formula  $C_{43}H_{60}O_8$  or  $C_{43}H_{58}O_8$ , the former agreeing the better with the results obtained by the analysis of the barium salt.

*Terpene (polymeride).*—By removing all traces of the resins  $\alpha$  and  $\beta$  from the alcoholic solution by repeated precipitation with lead acetate, separating excess of lead with sulphuric acid, distilling in steam to remove the alcohol, treating the residue with hot light petroleum until it ceases to extract anything, and cooling the solution, a straw-coloured fluid is obtained. The petroleum solution, after treatment with alcohol to separate the active principle and distillation, yields a thick oily straw-coloured substance, of bitter and somewhat pungent taste and aromatic odour. When heated, it volatilises with

partial decomposition. It is insoluble in potash, and its analysis leads to the conclusion that it is a hydrocarbon polymeric with terpene.

*Gingerol*.—The active principle has an alkaline reaction, and gives precipitates with lead, barium, and magnesium salts. When heated to  $100^{\circ}$ , it slowly loses weight, its colour darkening at the same time; boiling water and alkali decompose it, and it oxidises readily under the influence of nitric acid and chromic mixture. The facility with which it decomposes renders its isolation a matter of great difficulty. A more extended examination of this substance is to follow.

L. T. O'S.

**Derivatives of Photosantonin Acid.** By F. SESTINI and L. DANESI (*Gazzetta*, 1882, 82).—When this acid is distilled at the heat of a lead-bath in a current of inert gas ( $H$  or  $CO_2$ ), there is obtained, together with liquid hydrocarbons, a well-crystallised product, which, after purification, melts at  $94.5^{\circ}$ , dissolves in alcohol and in ether, and gives by analysis the formula  $C_{14}H_{20}O_2$ , and therefore consists of pyrophotosantonin acid:  $C_{15}H_{20}O_4$  (photosantonin acid) —  $CO_2 = C_{14}H_{20}O_2$ .—Pyrophotosantonin acid forms crystallisable salts. Its barium salt has the composition  $(C_{14}H_{19}O_2)_2Ba$ : hence the acid is monobasic, whereas photosantonin acid is bibasic.

When a mixture of equal parts of photosantonin acid and barium hydroxide is distilled in a vacuum over an open fire, there passes over a yellowish liquid, which, when dried over fused calcium chloride, distilled several times, and then fractionated over sodium, passes over for the most part at  $221.5$ — $223^{\circ}$ . The liquid thus obtained is colourless, has a faint odour like that of benzene-products, and gives by analysis the formula  $C_{13}H_{20}$ , which is confirmed by its vapour-density; exp. = 6.16; calc. 6.19. This hydrocarbon is isomeric with the dimethylamylbenzene of Bigot and Fittig, which boils at  $232^{\circ}$ , and with Jacobsen's methylpropyl benzene, which boils at  $243$ — $248^{\circ}$ .

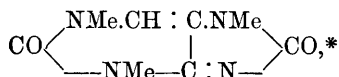
H. W.

**Nicotinic Acid from Pyridine.** By O. FISCHER (*Ber.*, 15, 62—64).—R. Laiblin (*Annalen*, 196, 163) suggested that nicotinic acid is a pyridinemonocarboxylic acid, and the author has now succeeded in proving this to be the case. Pyridine is converted into a *sulphonic acid* by heating it at  $320$ — $330^{\circ}$  with 3 to 4 times its weight of pure concentrated sulphuric acid in sealed tubes for a day. The *barium salt* is made by neutralising with barium hydroxide; it forms colourless needles with silky lustre, and mostly in nodules; it is very soluble in water, and contains 4 mols.  $H_2O$ , which are driven off at  $110^{\circ}$ . The *sodium salt* obtained from this forms small indistinct nodules, very soluble in water. Dried at  $100^{\circ}$ , and mixed with a third part of pure potassium cyanide, and distilled, it yields pyridine, a clear oil, which solidifies in the condenser, and finally a small quantity of a high-boiling yellow oil; ammonium carbonate and cyanide are also formed. The distillate is treated with soda, and extracted with ether, and on evaporating the ethereal extract, it leaves a crystalline magma of *pyridine cyanide*, which is purified by recrystallisation from light petroleum. It forms aggregations of needles (m. p.  $48$ — $49^{\circ}$ ), easily soluble in water, alcohol, ether, benzene, &c., less so in light petroleum.

It volatilises at the ordinary temperature. From a pyridine solution, it can be obtained in brilliant prisms 1 inch long. The hydrochloride crystallises in colourless needles. The platinocb chloride forms tufts of slightly yellow needles only moderately soluble in water. Pyridine cyanide is easily saponified by heating it with concentrated hydrochloric acid at 110—112°, producing ammoniac chloride and *nicotic acid*. Part of the latter separates out in granules on adding water to the crystalline magma left after driving off the excess of hydrochloric acid; the mother-liquor is concentrated, and the nicotic acid still in solution is separated by treatment with sodium acetate. The acid is purified by recrystallisation from water, melts at 228°, sublimes unchanged, and in no way differs from some nicotic acid prepared from quinoline.

D. A. L.

**Caffeïne.** By E. FISCHER (*Ber.*, 15, 29—33).—In order to confirm the suggestion made in a previous communication (this vol., 217) that the constitution of caffeine may be thus represented—



the author has further studied the constitution of caffoline with the following results:—

Caffoline,  $\text{C}_5\text{H}_9\text{N}_3\text{O}_2$ , is obtained from caffeine by successively removing one methylamine and two carbonic anhydride groups. By oxidation with chromic acid, it is decomposed into *ammonia* and *dimethylparabanic acid*. When, however, it is oxidised with potassium ferricyanide (in quantities equal to 1 atom O) a body is produced in the cold, which on warming breaks up into *monomethylcarbamide* and *methylloxamic acid*. The formation of these products from caffoline is thus represented:



On the other hand, oxidation with alkaline potassium permanganate gives *ammonia*, *carbonic anhydride*, and *dimethylloxamide*:  $\text{C}_5\text{H}_9\text{N}_3\text{O}_2 + \text{O} + \text{H}_2\text{O} = \text{NH}_3 + \text{CO}_2 + (\text{CO.NMeH})_2$ . From these reactions it is

evident that caffoline contains the group  $\begin{array}{c} \text{C—NMe—} \\ | \\ \text{C(NMe)N} \end{array} \text{CO}$ ; therefore

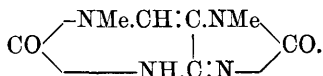
its probable constitutional formula is  $\begin{array}{c} \text{CH(OH).NMe} \\ | \\ \text{C(NHMe) : N} \end{array} \text{CO}$ , which is in

accordance with the above caffeine formula. By means of this formula, the author graphically illustrates the various stages in the formation of caffuric acid and caffoline from caffeine.

By the introduction of a methyl-group into theobromine (Strecker, *Annalen*, 118, 178) it is converted into caffeine. On oxidation with chromic acid caffeine yields *monomethyl-* (Maly and Hinterregger, *Monatsh. f. Chem.*, 1881, 87) and theobromine *dimethyl-parabanic acid*

\* The formula given in the abstract referred to is incorrect.—D. A. L.

(see ante). The author has repeated Rochleder and Hlasiwetz's (*Jahresb.*, 1850, 437) experiments on the action of chlorine on theobromine, and obtained *methylcarbamide* and *monomethylalloxan*. Theobromine therefore contains a monomethylated alloxan nucleus with one ammonia- and one methylamine-group. The relative positions of these groups are determined in the same way as in the case of caffeine, the ethyl-derivative being used instead of the simple bromo-compound. It is prepared by heating silver bromotheobromine with ethyl iodide at 100°. It resembles bromocaffeine. By boiling with alcoholic potash, it yields the ethoxy-derivative, and this, when warmed with hydrochloric acid, is converted into the beautifully crystalline *hydroxyethyltheobromine*,  $C_7H_6N_4O_2 \cdot Et.OH$ . As is the case with the corresponding caffeine-derivative, this is converted into a diethoxy addition-product by the action of bromine and alcohol, and in its turn is decomposed by warming with hydrochloric acid, producing alcohol, *methylamine*, and a compound homologous with apocaffeine. From these results it follows that the formula for theobromine is—



D. A. L.

**Action of Bromine on Caffeine.** By R. MALY and F. HINTEREGGER (*Monatsh. Chem.*, **3**, 85—91).—When dry bromine is added to a solution of caffeine in chloroform, an orange-coloured precipitate is formed (first observed by Schültzen, *Chem. Centr.*, 1868, 499, and afterwards by E. Fischer, *Ber.*, 1881, 637), which, when freed from excess of bromine by drying over quick-lime, forms an orange-red non-crystalline powder, having the composition of an addition-product, viz., *caffeine dibromide*,  $C_8H_{10}N_4O_2 \cdot Br_2$ . When, on the other hand, caffeine is heated in a sealed flask with bromine and water, the dibromide formed in the first instance disappears after a few hours, the liquid becoming decolorised, and yielding a white flocculent precipitate made up of slender non-lustrous needles, consisting of *monobromocaffeine*,  $C_8H_9BrN_4O_2$ . The quantity of this compound obtained varies according to the proportion of bromine used, 1 mol. caffeine yielding with 2 at. bromine 14 per cent. bromocaffeine, with 3 at. Br, 25 per cent., with 4 at. Br, 24.4 per cent., and with 6 at. Br, none, the compounds obtained in this last case being wholly products of oxidation, viz., *amic acid*,  $C_{12}H_{12}N_4O_7$ , and *dimethylparabanic acid* or *cholestophane*,  $C_3Me_2N_2O_3$ , which are also obtained, although in smaller quantities, when 2, 3, or 4 at. Br are used to 1 mol. caffeine.

Bromocaffeine is slightly soluble in cold water, more freely in hot water or hot alcohol; it dissolves also in strong acids, but is most readily dissolved by ether or chloroform. It is not altered by boiling with silver oxide and water, but is easily reconverted into caffeine by heating with water and zinc-dust.

H. W.

**Caffeine and Theobromine.** By R. MALY and R. ANDREASCH (*Monatsh. Chem.*, **3**, 92—110).—Rochleder, by boiling caffeine with hydrochloric acid and potassium chlorate, obtained a body resembling

alloxan, which he regarded as amalic acid (tetramethylalloxantin), but did not succeed in isolating it, as it decomposed during the evaporation of the liquid (*Annalen*, **63**, 201). E. Fischer (*Ber.*, **14**, 1912, also p. 218 of this volume) regards this body as dimethylalloxan, but he also has not been able to obtain it in the separate state. The authors of the present paper heated a mixture of 100 g. hydrated caffeine and 38.5 g. potassium chlorate in twenty small flasks with hydrochloric acid of sp. gr. 1.06, these proportions giving a quantity of active chlorine equivalent to 2 atoms of oxygen. The resulting solutions were then mixed, a stream of hydrogen was passed through the liquid to remove free chlorine and chlorous products, and a concentrated solution of acid potassium sulphite was added, whereby a heavy, white, scaly-crystalline powder was thrown down, the quantity of which went on increasing for two days; and on recrystallising this product from warm water, it was obtained in tabular crystals often measuring 25 mm.

This product is a compound of *dimethylalloxan with hydrogen-potassium sulphite*, represented by the formula  $\text{CO.NMe.CO.NMe.CO} \begin{array}{|c} \text{—C(OH)(SO}_3\text{K)—} \end{array}$ . It dis-

solves easily in warm, less readily in cold water, very slightly in alcohol, and not at all in ether. Heated on platinum-foil, it gives off fetid vapours smelling like allyl-compounds and burning uric acid; and on heating it in a tube, the crystals first turn red, then decrepitate, and give off purple, afterwards white vapours, condensing to a red oily ring and a white crystalline sublimate.

The aqueous solution of the compound gives with silver nitrate a white flocculent precipitate of silver sulphite; with lead acetate, a white heavy precipitate insoluble in acetic acid; with baryta-water, a copious white precipitate soluble in nitric acid; no precipitate with barium chloride. It does not give any blue coloration with ferrous sulphate and ammonia; but on treating it with hydrochloric acid, and leaving it to itself for a while, or evaporating it at a gentle heat, the same reagents produce a deep indigo-blue coloration.

*Crystallised or monohydrated dimethylalloxan*,  $\text{C}_6\text{H}_8\text{N}_2\text{O}_5 \cdot \text{H}_2\text{O}$ , or  $\text{CO.NMe.CO.NMeCO}$

$\begin{array}{|c} \text{—C(OH)}_2\text{—} \end{array} + \text{H}_2\text{O}$ , may be obtained from the compound just described, or more directly from the original solution, by extraction with ether. A second substance, to be described further on, is, however dissolved out at the same time; and to separate the two, the ethereal extract is freed from ether by distillation, and the residue is placed in a flat dish in a vacuum to remove the last traces of ether. There then remains a transparent, colourless, somewhat viscid, varnish-like mass, which when treated with a little water, soon becomes turbid, and in about an hour solidifies to a snow-white, crystalline pulp; and on stirring this up with a little cold water, and separating the liquid by pump-filtering, there remains a crystalline powder consisting of the second substance above mentioned as mixed with the dimethylalloxan in the ethereal extract, while the dimethylalloxan itself passes into the filtrate, as may be shown by treating a

portion of it with acid potassium sulphite, whereupon the saline compound above described separates out.

The solution left to evaporate over sulphuric acid, deposits after some days large transparent tabular crystals of hydrated dimethylalloxan, which effloresce and become opaque unless they are immediately removed from the liquid. They impart a red stain to wood and linen, also to the skin, but without producing any unpleasant odour. With ferrous sulphate and ammonia, the compound produces a fine deep indigo-colour. It may be easily recrystallised from water, over sulphuric acid, provided rise of temperature is avoided. The crystals are permanent in the air, but when left over sulphuric acid, they give off exactly 1 mol. water, and crumble to a white powder. When heated, they decompose with tumefaction and brown coloration, even at  $100^{\circ}$ .

Crystallised dimethylalloxan dissolves in alcohol, but is insoluble in ether. With ferric chloride and ammonia it forms a brown solution, showing that alloxan prevents the precipitation of ferric oxide. With cupric sulphate and potash it forms a blue solution. When heated in a small tube, it decomposes, turning brown and yielding a spangled sublimate. Its melting point is not determinable.

*Anhydrous dimethylalloxan*,  $C_6H_8N_2O_5$ , obtained by leaving the hydrate for a week over sulphuric acid, or in a vacuum, is a pale-yellow powder, which when brought in contact with a small quantity of water, quickly absorbs it, forming a crystalline cake of the hydrate, but is dissolved by a larger quantity. It is soluble in alcohol and in anhydrous ether. Its melting point cannot be determined. It turns yellow-brown at  $100^{\circ}$ , becomes viscous at  $105^{\circ}$ , and when more strongly heated yields a red oily sublimate.

*Apocaffeine*,  $C_7H_7N_3O_5$ , and *Caffuric Acid*,  $C_6H_5O_4$ .—Apocaffeine, which Fischer obtained by heating diethyl-hydroxycaffeine with hydrochloric acid (Abstr., 1881, 614), is also formed by direct oxidation of caffeine in the manner above described, being contained, together with dimethyl-alloxan, in the colourless varnish left on evaporating the ethereal extracts, and separable therefrom by water in the form of a crystalline powder (p. 630). Its formation in this manner is attended with separation of methylamine:  $C_8H_{10}N_4O_2 + H_2O + O_2 = C_7H_7N_3O_5 + CH_3.NH_2$ .

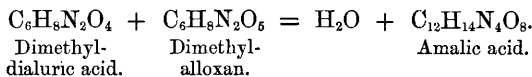
Apocaffeine dissolves sparingly in cold, more freely in warm water, with moderate facility in warm alcohol, and more readily in ether. It is partially decomposed by crystallisation from warm water, and is therefore more readily purified by dissolving it in ether, after drying over sulphuric acid, filtering if necessary, and mixing the filtrate with benzene. A strong milky turbidity is thereby produced, the liquid, however, soon clearing from above downwards; and after a few hours, the apocaffeine settles on the bottom and sides of the vessel in shining laminæ and needles. It does not lose weight over sulphuric acid in a vacuum. Heated in a test-tube, it begins to soften and stick to the sides at  $143^{\circ}$ , and melts completely at  $144$ – $145^{\circ}$ . It is soluble in alcohol and in chloroform.

Fischer, on boiling apocaffeine with water, observed evolution of carbon dioxide, and the formation of two new bodies, designated by

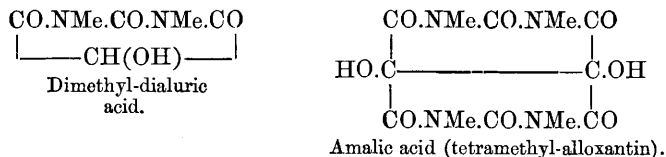
him as *hypocaffeine* and *caffuric acid*, the former crystallising out on evaporation, while the latter remained in the mother-liquor. Maly and Andreasch, on the other hand, obtain only one compound, viz., *caffuric acid*, and represent its formation by the equation  $C_7H_7N_3O_5 + H_2O = CO_2 + C_6H_5N_3O_4$ .

*Revision of the Formula of Amalic Acid: Dimethyl-dialuric Acid.*—*Synthesis of Amalic Acid.*—Rochleder's amalic acid (tetramethyl-alloxantin) is commonly represented by the formula  $C_{12}H_{12}N_4O_7$ , deduced from that of (hypothetically) anhydrous alloxantin,  $C_8H_4N_4O_7$ , by substitution of  $4CH_3$  for  $4H$ . This formula however, requires 44.44 per cent. C, 3.70 H, 17.29 N, and 34.57 O, and does not agree with the mean of Rochleder's analyses, viz., 41.97 C, 4.24 H, 16.46 N, and 37.27 O, which is more nearly represented by  $C_{12}H_{14}N_4O_8$ , requiring 42.10 C, 4.09 H, 16.37 N, and 37.44 O, and differing from the former by  $H_2O$ . This molecule of water cannot be regarded as crystal-water, for amalic acid dried in the exsiccator may be heated to  $120^\circ$  and above, without loss of weight, which in fact does not occur till decomposition sets in. Rochleder's formula has been further confirmed by the authors' analyses, the mean of which gave 41.90 C, 4.39 H, and 16.37 N.

When amalic acid is heated with water, and a stream of hydrogen sulphide is passed through the liquid, sulphur is separated; and on expelling the excess of hydrogen sulphide by a stream of hydrogen, a colourless solution is obtained containing dimethyl-dialuric acid:  $C_{12}H_{14}N_4O_8 + H_2S = S + 2C_6H_8N_2O_4$ . This liquid, when treated with oxidising agents ( $KMnO_4$  or  $NO_3H$ ), and even when left exposed in open vessels, is reconverted into amalic acid, a reaction exactly analogous to that by which dialuric acid is converted into alloxantin. That the compound  $C_6H_8N_2O_4$  obtained as above is really dimethyl-dialuric acid, is further proved by the fact that on mixing its solution with one of dimethyl-alloxan, a precipitate is formed consisting of amalic acid:—



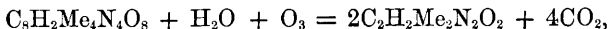
Dimethyl-dialuric acid and amalic acid may accordingly be represented by the following formulæ:—



*Decomposition of Amalic Acid by boiling with Water.*—The recrystallisation of amalic acid from water is attended, as already observed, with great loss; and when amalic acid is boiled for several hours with water, and the solution is then concentrated, there remains a white, neutral, crystalline mass easily soluble in water, which does not give



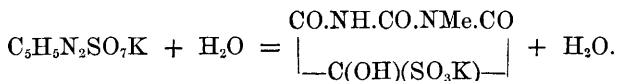
any particular reaction with iron-salts, alkalis, or baryta-water, or exhibit the reactions of parabanic acid. By recrystallisation from water, it is obtained in flat shining needles melting at  $208^{\circ}$ , and resolved by boiling with soda-ley into methylamine and oxalic acid. It is in fact dimethyl-oxamide, formed according to the equation—



and is the sole product of the reaction.

*Action of Chlorine, and of Potassium Chlorate and Hydrochloric Acid on Theobromine.*—When chlorine is passed into water holding theobromine in suspension, and the liquid is afterwards concentrated, a crystalline mass is obtained, exhibiting the reactions, not of amalic but of parabanic acid; and on recrystallising this product, limpid prisms are obtained, melting at  $147^{\circ}$ , resolidifying at  $102^{\circ}$ , and therefore consisting of methylparabanic acid, identical with that which is obtained by the action of chromic acid on theobromine.

A more definite reaction is, however, obtained by oxidising theobromine (3 mols.) with potassium chlorate (2 mols.) and hydrochloric acid, or by heating 2 pts. theobromine at  $50^{\circ}$  with 8 pts. dilute hydrochloric acid of sp. gr. 1.06, and gradually adding 0.907 pt.  $\text{KClO}_3$ . The liquid, filtered and freed by a stream of air from chlorous products, yields, when mixed with a strong solution of hydrogen potassium sulphite and left at rest for 24 hours, a crystalline mass, which must be freed from the remaining liquid by filtration, and recrystallised from warm water. In this manner large well-developed crystals are obtained, consisting of a compound of monomethyl-alloxan with hydrogen-potassium sulphite :—



The crystals, which have a vitreous lustre, are monoclinic prisms, exhibiting the oblique end-face and the clinopinacoid.

*Monomethyl-alloxan and Apotheobromine.*—On passing a stream of air through the product of the action of  $\text{KClO}_3$  and  $\text{HCl}$  on theobromine, then agitating it with ether, evaporating the ethereal extract, and removing the last traces of ether by evaporation in a vacuum, a viscid colourless varnish is obtained, which, when sprinkled with water, behaves exactly like the corresponding ether-extract of caffèine (p. 630), first becoming turbid, and then yielding a white crystalline powder. This latter consists of the compound analogous to apocaffeïne, and may therefore be named apotheobromine. It is but slightly soluble in cold water, gives off carbon dioxide on boiling, and melts at  $185^{\circ}$ . The filtrate from this compound gives the reactions of alloxan, and doubtless contains monomethyl-alloxan; but this body has not yet been obtained in the separate state.

*The Amalic Acid of Theobromine: Dimethylalloxantin,*



When the product obtained by the action of  $\text{KClO}_3$  and  $\text{HCl}$  on theobromine is treated with hydrogen sulphide, and then left to itself for

a while, it deposits, together with sulphur, crystalline scales of a body, which after filtration and recrystallisation from the smallest possible quantity of hot water, is obtained in iridescent laminæ and nodules. This body is the hydrated dimethylalloxantin above formulated, and exhibits the reactions of alloxantin itself, viz., violet coloration with caustic alkaline-leys and baryta-water, and red with ammonia. It turns red when heated to  $130^{\circ}$ , also on mere exposure to the air. It dissolves but very slightly, if at all, in alcohol and ether. H. W.

**Cinchonamine Cinchona Bark.** By G. PLANCHON (*J. Pharm. Chim.* [5], 5, 352—357).—The bark from New Grenada from which Arnaud obtained cinchonamine (this vol., 229), differs in many of its characteristics from the true cinchona barks; and although it may present some characteristics in common with the *China cuprea*, yet the differences between them show that each of them forms a distinct type. L. T. O'S.

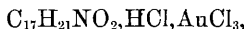
**Daturine.** By L. PESCI (*Gazzetta*, 1882, 59—61).—This alkaloid, extracted from the seeds of the thorn-apple (*Datura stramonium*), is generally regarded as identical with hyoscyamine from henbane (*Hyoscyamus niger*), but according to the author of this paper, the alkaloids obtained from these two sources are distinct. He prepares daturine by digesting bruised thorn-apple seeds for 24 hours at ordinary temperatures with twice their weight of ordinary alcohol holding in solution 3 g. tartaric acid in a litre; repeating the digestion with an equal quantity of the same liquid; then distilling off the alcohol; treating the brown viscid residue with water; filtering; concentrating to an extract; adding, after cooling, an excess of caustic soda sufficient to form a thick syrup; and agitating this syrup with commercial benzolin previously washed with dilute sulphuric acid. The benzolin used for this operation, after being freed from the dissolved alkaloid by dilute sulphuric acid, was again placed in contact with the extract of the seeds, and these operations were repeated four times. The whole of the dilute sulphuric acid which had been used to extract the alkaloid, was then rendered alkaline with ammonia and shaken up with chloroform, and this liquid, after concentration to about 10 c.c., was diluted with an equal volume of benzolin, and the mixture was left to evaporate, whereupon, after 24 hours, it deposited the alkaloid in concentric groups of thin white needles which were purified by pressure between bibulous paper, redissolution in chloroform, and dilution with benzolin. By this treatment  $\frac{4}{5}$  cgrs. of seeds yielded 1.9 cgr. of pure daturine.

The base thus prepared melted at  $106\text{--}108^{\circ}$ , agreeing therein with Ladenburg's determination, whereas a specimen obtained from Schuchardt's factory liquefied at  $97\text{--}99^{\circ}$ , and another from the Pharmacie Centrale de la France at  $109\text{--}110^{\circ}$ . The *hydrochloride* and *sulphate* crystalline in thin colourless needles having a nacreous lustre. The *aurochloride*,  $C_{17}H_{23}NO_3 \cdot HCl \cdot AuCl_3$ , crystallises in groups of light yellow needles, melting at  $137\text{--}139^{\circ}$ , whereas Ladenburg found the melting point to be  $159^{\circ}$ .

Daturine behaves like atropine with all reagents, excepting platinic chloride. A 1 per cent. solution of atropine in acetic acid gives with

this reagent a yellow crystalline precipitate, whereas it is not precipitated by a solution of daturine of equal strength.

Daturine is converted by nitric acid into a base exhibiting all the characters of *apoaotropine*, yielding an amorphous aurochloride,



very slightly soluble in water and melting at  $106-108^\circ$ . The same base heated at  $90-100^\circ$  with baryta-water is resolved into atropic acid and tropine. H. W.

**Extract of Aconite and the Alkaloid of *Aconitum paniculatum*.** By E. L. CLEAVER and M. W. WILLIAMS (*Pharm. J. Trans.* [3], 12, 722—723).—Extract of aconite is prepared from two different plants, *Aconitum Napellus* and *Aconitum paniculatum*, and some specimens of the commercial extract fail to produce the characteristic tingling sensation and numbness of the tongue and lips. On examining the extract from the *Aconitum paniculatum*, as well as its leaves and stems, it was found to contain an amorphous substance totally free from aconitine, but possessing the properties of an alkaloid and resembling picroaconitine, which T. B. Groves has obtained from the roots of the same plant.

The extract of *A. paniculatum* is of a green colour and slightly bitter taste, but produces none of the after-effects of the extract of *A. Napellus*, which has a brown colour. L. T. O'S.

**Ptomaines.** By T. HUSEMANN (*Arch. Pharm.* [3], 19, 415—424).—Selmi has, in two cases, found ptomaines in bodies of persons dying from acute arsenic poisoning. In the first case the body was exhumed 14 days after burial, and appeared well preserved, arsenic being present in abundance. By extraction with ether a minute quantity of a body, giving the principal reactions of the alkaloids, was obtained, but in insufficient quantity to examine for arsenic.

Shortly afterwards he was able to extract from a body disinterred a month after death a larger quantity of a readily crystallisable ptomaine, which gave precipitates with tannic acid, iodised hydriodic acid, gold chloride, mercuric chloride, and picric acid, but no precipitate with platinic chloride or potassium dichromate. This ptomaine, which Vella showed to be very poisonous to frogs, was found to be non-arsenical.

By keeping a pig's stomach in a solution of arsenious acid in a cool room, Selmi succeeded in producing a volatile and a fixed arsine, both highly poisonous to frogs.

The author considers that as a volatile arsenic compound is here produced, other bases, or the same base, might occur from the action of the size in arsenical wall-papers in presence of moisture.

Selmi has also shown the presence of arsenical organic bases in the urine in cases of chronic arsenical poisoning. F. L. T.

## Physiological Chemistry.

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**Elimination of Gaseous Nitrogen by Animals.** By J. SEEGEN and others (*Bied. Centr.*, 1882, 23—28).—Seegen and Nowak assert that animals eliminate gaseous nitrogen by the lungs (Abstr., 1880, 272), and that this nitrogen is formed from the albuminoids. Pettenkofer and Voit (Abstr., 1882, 238) do not believe this statement, but think that the nitrogen found by analysis was due to imperfections in the methods employed. H. Leo has repeated the experiment with improved apparatus and methods, and found that the amount of nitrogen diminished as each improvement was introduced; he therefore believes that if any nitrogen is eliminated in this way, which is very problematical, the amount is so small as to be of no consequence. E. W. P.

**Feeding with Milk.** By CAMERER (*Bied. Centr.*, 1882, 62).—Two children were fed with milk and coffee for five days, with the following results:—

	Expt. I.	Expt. II.
1 part albuminoids developed fat and lactose	2·2	2·2
100 parts water appeared as urine . . . . .	8·69	9·28
100 „ dry matter appeared as dried fæces	7·1	4·4
100 „ nitrogen appeared as { in urine ..	83·7	78·0
nitrogen . . . . . { in fæces ..	5·5	3·4
{ in both . . .	89·2	81·4
100 parts fat appeared in fæces as fat . . . . .	2·8	2·8

E. W. P.

**Feeding Milch Cows with Cotton Cake.** By M. SCHRODT and H. PETER (*Bied. Centr.*, 1882, 91—94).—Full details of the experiments are given, and the conclusions drawn are that decorticated cotton cake raises the amount of dry matter and fat, confirming the experiments of Pogge and others (this vol., 321). E. W. P.

**Fattening of Pigs.** By P. SCHNEIDER and others (*Bied. Centr.*, 1882, 94—96).—Accounts of successful experiments in the fattening of pigs with a mixture of barley, maize, potatoes, and skim milk; a satisfactory return was gained for the various expenses occasioned. E. W. P.

**Phosphoric Acid in the Urine of Graminivora.** By M. C. LEEUW (*Bied. Centr.*, 1882, 85).—The appearance of phosphates only in the dung of Graminivora is due to the alkalinity of the urine and to the lime present in the food. If then the lime given in the food be reduced, phosphates should appear in the urine. Such seems to be a correct surmise, for when oxen were fed on distillers' waste, together with a minimum quantity of hay, &c., phosphoric acid was found to the amount of 1·13 grams per litre. E. W. P.

**Occurrence of Ammonium Magnesium Phosphate in a Sample of Old Urine.** By H. SCHWANERT (*Ber.*, 15, 37—39).—The urine was found in a corked bottle in a coffin, with a human skeleton, under the pavement of a street, which had previously been a churchyard. It was a dark brownish-yellow liquid, with alkaline reaction, in which were suspended three crystals and a sediment. There was no urea present, it being all converted into ammonium carbonate. The sediment consisted of calcium carbonate and ammonium amidobarbiturate. The crystals were ammonium magnesium phosphate.

D. A. L.

**Behaviour of some Ferments in the Animal System.** By FALK (*Bied. Centr.*, 1882, 138).—Emulsin is unaffected by saliva, pancreatic juice and pepsin, but it is destroyed by gastric juice and bile. The intestinal fluids decompose amygdalin. The decomposition of amygdalin by pancreatic juice is feeble and inconstant, whereas saliva acts more distinctly. The ferment in saliva is not affected by pepsin, but it is by gastric juice and bile, with formation of a sediment; saliva diastase resists fermentation better than emulsin; the like properties are possessed by malt diastase. The poison of putrefaction is not destroyed by any of the digestive juices, or by hydrochloric acid.

E. W. P.

**Tuberculosis Poison.** By H. TOUSSAINT (*Bied. Centr.*, 1882, 96).—Animals inoculated with tuberculosis poison die of a certainty, and the poison becomes the more virulent each time that it is transferred by inoculation from one patient to another.

E. W. P.

**Researches on Lupine Sickness in Sheep.** By ROLOFF and others (*Bied. Centr.*, 1882, 97—100).—The symptoms of sickness produced by lupines partake in part of the character of acute jaundice, and of phosphorus poisoning; convalescence seldom occurs.

The spleen, kidneys, heart, and muscles are all affected, and the sickness afflicts horses, dogs, and goats, as well as sheep.

The poison is insoluble in alcohol, ether, and glycerol, and but slightly soluble in acidulated water, whereas it is readily dissolved by alkalis; it appears to be a glucoside or organic acid. At 120°, and under 1—1½ atmosphere pressure, the virulence of the poison is reduced, and the poison itself passes over with the vapour of boiling water. Long keeping in dry places seems to intensify its action.

Farmuth thinks that the harmful action of lupines is a secondary result following on a weakened or disordered state of the digestive organs; he cites cases in which sulphur and cream of tartar have been given with good results. Reichert holds similar opinions, and adds that the greatest harm is done when lupines are given suddenly and in large quantities. He recommends 0.3—0.6 gram calomel, 1.25—1.5 grams aloes, and 2.36—2.5 grams sodium borate, mixed up with linseed meal as a dose, and that salt and easily digestible foods be given. Ketti has patented a process which destroys the poison; the lupine hay is moistened with acidulated water (1 litre H<sub>2</sub>SO<sub>4</sub> to 2000 litres H<sub>2</sub>O).

E. W. P.

## Chemistry of Vegetable Physiology and Agriculture.

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**Electrical Researches on Plant and Animal Forms.** By A. J. KUNKEL (*Bied. Centr.*, 1882, 28—30).—The absorption of water by porous bodies is accompanied by electric currents. When a porous earthenware cell is partly filled with water, and a current completed through a galvanometer by means of electrodes in the water and in contact with the outer wall of the cell, a current passes. The intensity continually diminishes, until it finally ceases, and then a current begins in the opposite direction from the cell wall through the water. This reversal of current is due to the incomplete state of saturation of the walls of the cell. These phenomena are employed by the author to account for various electric phenomena observed in plants.

*Electromotive Action of the Upper Surface of Green Leaves.*—The difference of tension of the various parts was determined by a systematic method of contact over the whole surface, with the result that the leaf-nerves are generally positive towards the rest of the leaf, but the direction of the current is reversed if the spot on the leaf where the electrode is placed is wetted before the other electrode is placed on the nerve. Also a spot long moistened is positive towards one freshly wetted. When the electrodes rest on the epidermis of a plant, and a wound is made near the electrode, then that electrode will be negative to the other. The same result is obtained by bending the plant, and the current formed is the more intense the greater the amount of bending, the electrode near the bend being negative to the other. Sometimes plants also show the existence of electric currents in their structure, which when the plant moves cause the galvanometer needle to oscillate.  
E. W. P.

**Electromotive Properties of the Leaf of *Dionæa*.** By J. B. SANDERSON (*Proc. Roy. Soc.*, 33, 148—151).—The author has investigated the immediate and subsequent electrical results of excitation of the leaf of the *Dionæa*, which have previously been examined by Munk, Kunkel, and the author himself.

It is found that at the moment of excitation (whether mechanical or electrical), the *under* surface of the lobe of the leaf is electronegative to the upper surface, the difference of potential reaching its maximum about half a second after excitation; it then rapidly decreases, until the *upper* surface is ultimately electronegative to the lower, and this after effect remains constant for some time. With a current not much more than adequate, excitation occurs at the moment of closing the current, but none occurs on breaking the circuit unless the current be sufficiently strong. The author considers (1) that the difference of potential is due to the electromotive forces which reside in the living protoplasm of parenchyma cells in contact with one another, and in different states of physiological activity; (2) that the second phase of excitation is probably dependent on the diminution of turgor of the excited cells arising from a migration of liquid; (3) this explanation cannot be accepted for the phenomena of the first phase, the sudden accession

and rapid propagation of which show that it is probably analogous to the "negative variation" or "action current" of animal physiology.

V. H. V.

**Influence of the Electric Light on Vegetation.** By C. W. SIEMENS (*Ann. Agronomiques*, 7, 456—462; from *Agric. Gazette*, Sept. 12th, 1881).—This paper contains an account of experiments made during the winter 1880–81, the results of which were described in a paper read before the British Association (1881). A 6-horse high pressure steam engine was employed to drive two Siemens dynamo-electric machines, each of which supplied a 4000 candle Siemens electric lamp. One lamp was placed inside a greenhouse, and the other suspended at a height of 4—5 yards above the greenhouse. From Oct. 20, 1880, to May 7, 1881, they were lighted at 5 or 6 o'clock in the evening and extinguished at daybreak. The light placed above the greenhouse was enclosed in a lantern of transparent glass, whilst that placed inside the greenhouse was unprotected. The temperature was maintained as nearly as possible at 15°.

All the plants exposed to the direct rays of the electric light quickly drooped and withered; those exposed only to the light of the lantern preserved their healthy appearance, and were stimulated in growth. When the light was transmitted through glass of different colours, the following effects were observed:

Under the white glass, the plants made rapid progress and vigorous growth; under yellow glass, the plants, although healthy, were noticeably inferior to the preceding; under red rays, the growth was moderate, and the leaves took a yellowish tint; the plants under blue rays were still less vigorous, and those exposed to the naked light were withered, blackened, and stunted. Under the influence of the electric arc protected by a transparent globe, peas sown at the end of October were gathered ripe on February 16th; ripe raspberries were gathered March 1st, and excellent strawberries on February 14th, from plants placed in the greenhouse on December 16th. Wheat, barley, and oats, sown in the open air near the electric lamp, were greatly retarded in germination by the snow, but afterwards grew rapidly, and yielded ripe seed by the end of June, having been assisted by the electric light up to the beginning of May.

Some of the peas gathered on February 16th were sown on the 18th, and produced healthy plants. Bananas and melons of superior size and flavour were ripened in early spring. The author concludes that as far as his observations on a large number of plants enables him to judge, plants do not seem to require nocturnal and hibernal repose, and their health is in no way injured by its deprivation, whilst growth and ripening are stimulated in a very marked degree. The rest of the paper is devoted to devices for reducing the cost of the electric light as applied to horticulture by transmitting the electric current during the day to different parts of the premises, where it actuates electromotors employed for pumping water, sawing wood, chaff cutting, root pulping, &c.

J. M. H. M.

**Vegetation in an Atmosphere rich in Carbonic Anhydride.** By P. P. DÉHÉRAIN and L. MAQUENNE (*Ann. Agronomiques*, 7, 385—

406).—The authors' experiments consisted in growing young plants, previously weighed, under three bell-jars. One of these communicated with the air simply by means of a cork and glass tube; the second was kept constantly supplied with a current of air by means of a water-pump; and the third was connected with apparatus by which a measured volume of carbonic anhydride could be introduced at will, and by which samples of air could be withdrawn for analysis. The plants experimented on were kidney-beans still retaining their cotyledons, colza, *Ageratum ceruleum*, chrysanthemums, and tobacco plants. The air of the third bell-jar was analysed from time to time after introduction of the carbonic anhydride, and as soon as the supply was exhausted, a fresh quantity was admitted.

The experiments lasted from a few days to over a month. The quantity of carbonic anhydride introduced was from 3 to 4 per cent. of the air inside the bell-jar.

The results varied a good deal in the different experiments, but allow the following general conclusions to be drawn:—

An atmosphere rich in carbonic anhydride enables plants to withstand heat and drought better than normal air. Very much more starch is found in the leaves of plants grown in excess of carbonic anhydride, and in some cases the total weight of the plant is largely increased. In all cases the plant is yellower than one grown in normal air. Greenness can be restored either by dosing the plant with potassium chloride or by removing it to normal air; at the same time the excess of starch disappears from the leaves. A tobacco-plant grown in calcined soil in an atmosphere rich in carbonic anhydride, was found to contain an excess of carbon over that contained originally in the plant, and that resulting from the carbonic anhydride introduced. The source of this excess was shown to be carbonic anhydride derived from slow combustion of the organic matter of the uncalcined earth placed under the bell-jar at the same time.

J. M. H. M.

**Formation of Starch in Plants.** By DETMER (*Bied. Centr.*, 1882, 110).—The presence of organic acids such as citric acid, renders the action of diastase on starch in the plant more rapid. In those plants which require much salts—say nitrates, whose acid is assimilated by them in larger amount than the base, the acid character of the cellular fluid is reduced; on the other hand, the fluid is more acid when potassium or ammonium chlorides are used, for the bases are taken up in larger quantities than the chlorine. The question has been frequently raised as to whether diastase is a distinct combination, or whether the transformation of starch is caused by albuminoids present as such in the cells, and acting, under certain conditions, on the starch. The author considers diastase to be the acting substance, and distinct from albuminoids, as it can pass through cell-walls, whereas albuminoids cannot.

E. W. P.

**Increase of Root and Leaf of Sugar-beet during Growth.** By H. BRIEM (*Bied. Centr.*, 1882, 34—38).—The statistics employed in this paper are collected from various districts in France and Germany; the periods to which attention is directed are the decades of



the months of May to October. The results are: there is a continuous increase during the whole growth; during May and June it is slow, but very rapid in July and August, whilst in September and October it is greatly reduced. The weight of the roots continuously increases, the increase being greatest in August; the leaves, however, reach the maximum weight in July, and decrease in September and October. Roughly speaking, the increase of root-weight is in inverse ratio to that of the leaves, for at the beginning of the season we find that for 100 grams roots there are 989 grams leaves, and 100 of leaves correspond with 10 of roots in May; but in August we find 60 of leaves to 100 of roots, or 166 roots for 100 of leaves: and in October 28 of leaves for 100 of roots, or 352 of roots for 100 of leaves. E. W. P.

**Internal Growth of Potatoes.** By M. LEBL (*Bied. Centr.*, 1882, 67).—Some potatoes kept in a cellar, and from which the sprouts were removed as fast as they formed, were split open after a time and found to contain small but perfectly formed tubers. E. W. P.

**Influence of Light on the Formation of Red Pigment.** By A. BATALIN (*Bied. Centr.*, 1882, 65).—White light is necessary for the formation of the red pigment in *Polygonum fagopyrum*, and the depth of the colour is dependent on that of the light, also a moderate temperature is requisite for its production. E. W. P.

**Relation between the Moisture of the Soil and the Germination of Sugar-beet Seeds.** By H. BRIEM (*Bied. Centr.*, 1882, 80).—When the soil contains 17—7 per cent. of moisture, the conditions for normal germination are attained, but on either side of this boundary germination is retarded, and if the moisture is below 5 or above 22 per cent. it does not take place at all. If the seed has been previously soaked in water, it will germinate in soil with 5 per cent. moisture, but will not sprout through the soil. E. W. P.

**Alteration in Plants when Grown on Heated Soils.** By E. PRILLIEUX (*Bied. Centr.*, 1882, 64).—Beans and pumpkins were grown in soil artificially heated from below; the seed germinated well, but the seedlings grew to no length, and appeared swollen, with the result that rents were formed in the stem; the direction of the rifts was not lengthways, but diagonal, indicating that the seat of the evil was not on the surface. Examination showed that the pith-cells were very much enlarged, in fact almost quadrupled in diameter. The cause of the changes observed was hypertrophy of the cells extending to the core. E. W. P.

**Respiration of Plants.** By J. BORODIN (*Ann. Agronomiques*, 7, 462—467).—A branch cut from a living plant, when placed in the dark, exhales carbonic anhydride at a continually decreasing rate, and the author explains this by the exhaustion of the stock of ready formed carbohydrates which supply the carbonic anhydride given off in respiration; after insolation of some hours' duration in an atmosphere rich in carbonic anhydride, the respirative power is fully restored, according to the author, by the assimilation of fresh sup-

plies of carbohydrates. Richawi disputes this conclusion, and contends that the apparent renewal of respiration is due to the giving off of carbonic anhydride mechanically absorbed by the plant tissues during their sojourn in an atmosphere rich in that substance. In this paper, the author adduces experiments which show that his original interpretation of the phenomena is the correct one.

J. M. H. M.

**Chemical Composition of Mildew Fungus.** By N. SIEBER (*J. pr. Chem.* [2], **23**, 412—421).—The specimens of mildew analysed were obtained from solutions of varying composition, the one consisting essentially of sugar and gelatin, the other of sugar and ammonium chloride. After washing the fungus with water and drying, it was extracted with ether and alcohol; a crystalline substance was obtained from the extract, but its composition has not been satisfactorily determined. The portion insoluble in these solvents consists essentially of albumin and cellulose. The following table contains the proximate analyses of these two varieties of mould: I, obtained from sugar and gelatin, and consisting of *Aspergillus glaucus*, *Penicillium*, and *Mucor mucedo*; II, obtained from sugar and ammonium chloride, consisting essentially of *Aspergillus glaucus* :—

	I.	II.
Soluble in ether .....	18·70	11·19
Soluble in alcohol.....	6·87	3·36
Ash.....	4·89	0·73
Albumin.....	29·88	28·95
Cellulose .....	39·66	55·77
	100·00	100·00

P. P. B.

**Composition of Buckwheat.** By M. G. LECHARTIER (*Ann. Agronomiques*, **7**, 376—385).—The author has made comparative analyses of three crops of buckwheat grown under different conditions: (1) and (2) grown at Cesson in a sandy soil in 1879 and 1880; (3) grown at St. Jacques in a gravelly conglomerate. The air-dried plant contained 10—15 per cent. water; the analyses were executed in samples dried at 100°.

	Cesson, 1879.	Cesson, 1880.	St. Jacques, 1880.
Proportion of straw to grain .....	0·920	1·585	1·640
Ash per cent. of straw.....	7·968	9·089	10·200
Ditto after deducting CO <sub>2</sub> .....	6·234	7·743	8·903
Ash per cent. of grain (free from CO <sub>2</sub> )..	1·855	2·350	2·171

The composition of the straw and grain in parts per 1000 was as under. The composition as given in Wolff's table is also cited for the sake of comparison :—

	Dry straw.			
	Cesson, 1879.	Cesson, 1880.	St. Jacques, 1880.	Wolff.
Ash .....	79·68	90·89	89·08	61·14
Nitrogen .....	8·90	12·29	11·55	15·47
Potash .....	14·08	33·95	44·90	40·57
Soda .....	1·32	1·32	0·60	1·31
Lime .....	22·37	16·90	11·77	11·31
Magnesia .....	10·11	5·78	4·34	2·26
Oxide of iron .....	1·11	1·28	1·00	—
Phosphoric acid .....	2·07	6·39	11·64	7·26
Silica.....	3·01	0·47	1·68	3·33
Sulphuric acid.....	2·35	1·94	2·69	3·21
Chlorine .....	6·40	9·32	15·41	4·76

	Dry grain.			
	Cesson, 1879.	Cesson, 1880.	St. Jacques, 1880.	Wolff.
Ash .....	18·57	23·50	21·71	10·71
Nitrogen .....	19·13	23·17	22·06	16·76
Potash .....	5·06	6·15	6·49	2·44
Soda .....	0·78	0·18	0·13	0·70
Lime .....	1·12	2·39	1·04	0·35
Magnesia .....	3·22	3·54	3·80	1·40
Oxide of iron .....	0·12	0·07	0·05	—
Phosphoric acid .....	6·79	10·22	9·65	5·13
Silica.....	0·00	0·07	0·00	—
Sulphuric acid.....	0·63	0·92	0·49	0·23
Chlorine .....	0·12	0·15	0·14	0·23

These figures show that the composition of the grain varies within narrow limits in correspondence with a large variation in the composition of the straw, especially as regards potash, chlorine, and phosphoric acid. In one sample of straw, for instance, the proportion of  $P_2O_5$  is quintupled and exceeds that in the grain. A crop of buckwheat removes more from the soil than a crop of wheat with an equal weight of grain; and it must be considered as an exhausting crop when luxuriant development of its foliage is encouraged by atmospheric conditions. The phosphoric acid, potash, and nitrogen removed in the straw is, however, returned as manure. The straw differs entirely from that of wheat in not suffering impoverishment during the ripening of the grain.

J. M. H. M.

**Composition of some Forest Seeds.** By L. JAHNE (*Bied. Centr.*, 1882, 106).

	Abies excelsa.	Pinus Laricio.	Pinus silvestris.	Pinus Cembra.	Larix europ.
H <sub>2</sub> O.....	7·82	9·66	9·64	10·22	10·81
Ether extract.....	22·99	31·68	33·16	25·76	11·43
Fibre .....	32·01	29·27	20·19	42·26	58·44
Albuminoid.....	20·25	18·76	28·63	5·01	4·51
Ash .....	6·29	3·05	6·58	1·48	2·57
Resin and nitrogen- free extract	18·46	7·24	11·14	25·49	23·05

	Robinia pseudo- acacia.	Fraxinus excelsior.	Betula verrucosa.	Acer campestre.
H <sub>2</sub> O.....	11·34	8·84	10·53	9·74
Ether extract.....	12·11	29·19	20·40	32·50
Fibre .....	14·96	7·52	27·21	9·57
Albuminoid.....	37·15	13·65	14·40	26·67
Ash .....	4·61	3·20	4·23	4·98
Resin and nitrogen- free extract	31·71	46·44	33·76	26·28
Sugar .....	—	3·74	2·23	2·07
Dextrin .....	—	16·41	9·69	—

Starch was not found in any case.

E. W. P.

**Peat-moss from Bad Steben near Hof.** By E. REICHARDT (*Arch. Pharm.* [3], 19, 424—428).—The author examined two samples of the above with the following results per cent. :—

	I.	II.
Moisture.....	81·30	73·74
Nitrogen .....	1·54	1·80
Sulphur (other than as sulphuric acid).....	1·20	0·18
Sulphuric acid (in the ash) .....	0·39	3·55
Iron oxide .....	4·54	7·61
Alumina.....	—	4·95
Alkali salts .....	1·71	0·76
Sand and clay .....	—	10·66
Total ash .....	7·06	24·37

} Determined on the  
dried substance.

By distilling samples with 5 per cent. caustic soda solution, alkaline distillates were obtained containing ammonia and methylamine. By distilling with 5 per cent. sulphuric acid solution, acid distillates were obtained containing formic, acetic, and traces of butyric acid.

Benzene extracted 1·2 per cent. of solids from the dry peat.

F. L. T.

**Nitrogenous Constituents of Plants.** By E. SCHULZE (*Chem. Centr.*, 1882, 89).—Asparagine is present in a large number of plants, and can be extracted easily from very impure solutions in well-formed crystals. Glutamine is contained in the juice of beetroot and in gourd sprouts, glutamic acid being formed on boiling beetroot juice and extracts from gourd sprouts with hydrochloric acid. However, the author has not yet been able to isolate glutamine, and it is still questionable whether this amide is homologous with asparagine. With regard to the amido-acids contained in vegetable juices, tyrosine and next asparagine are the least soluble, so that their separation can be effected with great ease. Leucine and its homologues have a solubility different in the impure state from what it is after purification; these bodies are therefore not separated so readily; moreover they are deposited in non-crystalline masses from their extracts, rendering it difficult to distinguish them. It is best to allow them to crystallise from alcoholic solutions, and to purify the crystals by recrystallisation from ammoniacal alcohol. The author obtained from lupine sprouts an acid having the composition  $C_9H_{11}NO_2$ , and yielding benzoic acid on oxidation. It is probably a phenylamidopropionic acid. When heated in a glass tube, it splits up into water, carbonic anhydride, a crystalline residue, and an oily distillate solidifying on cooling to a crystalline mass. The latter is the carbonate of a base having the composition  $C_9H_{11}N$ , and yielding benzoic acid on oxidation. It is probably a homologue of benzylamine. The author further shows that this phenylamidopropionic acid is intimately connected with tyro-leucine, ( $C_{14}H_{22}N_2O_4$ ), found by Schützenberger among the decomposition-products of albumin. This body yields the same decomposition-products, and also amidovaleric acid. Schützenberger assumed that tyro-leucine is a compound of amidovaleric acid and a body having the formula  $C_9H_{11}NO_2$ . Probably this is correct, and the body  $C_9H_{11}NO_2$  is identical with the above-mentioned phenylamidopropionic acid. From young leaves of the plane tree, the author obtained asparagine and a body having the formula of allantoin,  $C_4H_6N_4O_3$ , and resembling it in chemical properties.

D. B.

**Steeping of Barley.** By ULLIK (*Bied. Centr.*, 1882, 40—42).—It is generally supposed that hard waters remove less of the constituents from barley than soft waters; therefore, to determine the correctness of this supposition, barley was steeped in distilled water, River Elbe water, a temporary hard well-water, and in two samples of water containing calcium sulphate. All the waters remove more potash than distilled water does, but soda is removed in the greatest amount by the gypsum and distilled water, and magnesia by the hard waters, as also the lime; but no great difference is found as regards the phosphoric acid. The following explanation of the removal of the bases is given:—The phosphoric acid exists as an insoluble compound with lime and magnesia, and the rest as soluble, a primary and secondary potassium compound, and primary calcium and magnesium phosphate. Now, as the barley contains free acid, it follows that a conversion of the secondary potassium phosphate into primary takes place; this phosphate is then precipitated by the calcium carbonate in the hard water, if the carbonic anhydride be removed.

Soft water removes more organic matter from barley than hard, but the amount is small; whilst carbohydrates are removed most, nitrogenous matter is dissolved out the least by soft water; finally, it is found that the duration of steeping has a greater effect on the barley than the quality of the water.

E. W. P.

**Contributions to the Phylloxera Question.** By COSTE and others (*Bied. Centr.*, 1882, 108—110).—Mayet considers that the moisture of the air has great influence on the production of the winter egg of the phylloxera, dry autumns being unpropitious. Boiteau gives methods for employing carbon bisulphide. J. D. Catta mentions the harm done to vegetation by the use of the above chemical, and the means to avoid this damage. Henneguy uses 25 grams carbon bisulphide per square meter, without doing harm to the vines.

E. W. P.

**Researches on the Influence of the Distance between the Seed Sown on the Growth and Quality of the Crops.** By E. WOLLNY (*Bied. Centr.*, 1882, 112—129).—The various factors which effect the growth of a crop are here carefully considered, and numerous tables are appended, which are of much interest and value. Taking the crop as a whole, the maximum yield from a certain area is dependent on the quantity of seed sown; by thinner or thicker sowing the yield is less. The quality of the crop is best when the plants are far apart, *i.e.*, the grains are heaviest. Straws and fodder increase as the space decreases. The power of production possessed by a plant increases with the space allotted. Still the productiveness of any one plant bears no constant relation to the space in which it grows; for although the weight of the yield increases up to a certain extent as the space increases, yet the extent is different for each variety and kind. The increase of yield is not regularly proportional to the increase of ground space, but is greatest at first, and then gradually becomes less. Experiments were also instituted to discover what other influences were at work on the productivity of plants besides that exerted by the ground space. This set of experiments was made in circular vessels of like depth, but of varying diameter, with the result that the yield of the plant whose growth above ground was unrestricted increases with the ground space, but not proportionally, being in a somewhat lesser ratio to the latter. This corroborates the results of Haberlandt, who found the yield to be relatively larger the smaller the space allotted to each plant. The reasons given are, that when the plants are crowded together, the roots come into closer contact with the nutriment in the soil. Of all the causes which lower the yield when the plants are close together, the most important is light, which, being in a measure cut off, does not cause assimilation to be perfect; then the internodes are unnecessarily increased, and wood is not properly formed. The next important factor is warmth. Soils well covered with vegetation are always much cooler than other soils during hot weather, and not only is the soil cooler, but the circulating air, also under like conditions, is cooler, and nocturnal radiation is greater the closer the plants are together. When the plants stand thickly, they shelter the soil from slight rainfall, and although

they hinder the evaporation of water from the soil, yet they withdraw and transpire an excess of water, the result being that the roots have not a sufficiency. It appears also that the space which should be apportioned to each plant varies with each variety of the plant. Another set of experiments shows that the richer the soil is and the better its condition, the less will be the seed required to obtain a maximum crop, and this quantity must be reduced if the soil soon dries; but on the other hand, if the soil is heavy, then a larger amount must be sown. In climates which are against the growth of any crop, an excess of seed must be used. When large seeds are sown at such a distance from one another as to produce the maximum yield, then the same weight of small seeds in the same space will produce a smaller yield. If the plants from small seeds are producing their maximum yield, then a like quantity of large and small seeds will on the same ground produce a like yield; for in this case the plants from large seeds cannot completely utilise the soil. When the limit of space is overstepped, then small seeds will be more prolific than large. Seed should be sown as early as possible, otherwise the quantity required to produce a crop will have to be increased.

As regards the composition of some plants as affected by the ground space, the author finds that the nitrogen and ash in maize increase as the space diminishes; that, on the other hand, these two constituents in buckwheat and soja bean increase with the space; that in general the fibre is increased by crowding the plants. It is advantageous to plant sugar-beets close together, as then the yield of sugar is increased, and the albumin diminished in quantity. E. W. P.

**Examination of Oats.** By R. v. MOSER (*Landw. Versuchs.-Stat.*, 27, 209—213).—Difference of opinion as to the relative values of mountain and lowland oats in the rearing of young horses, caused the Agricultural Department of the Austrian Government to order a thorough examination of numerous specimens of both kinds. Twenty-two samples were carefully selected and placed in the author's hands for analysis. He had them examined mechanically and chemically, and gives the results in tabular form; but the figures vary so much amongst the members of each group, that no reliance can be placed on them as guides of the value of the two classes, the individual members of each showing greater differences amongst themselves than does the mountain class from the lowland. J. F.

**Cultivation of *Vicia Villosa*.** By H. ECKERT and others (*Biedl. Centr.*, 1882, 110).—A mixture of winter and summer rye with *Vicia villosa* was sown and manured with blood manure. The vetch suffered from the drought, and was much choked by the winter rye; but after a rainfall, it was enabled to grow strongly and produced a fair crop. Haage and Schmidt also recommend a similar mixture, as this kind of vetch on sandy soil and in dry seasons produces better crops than other fodder-plants. E. W. P.

**Digestibility of Certain Oil-cakes.** By E. WOLFF and others (*Landw. Versuchs.-Stat.*, 27, 216—240).—The oil-cakes commonly

used for feeding cattle in Germany, viz., linseed, rape, palm-nut, and undecorticated cotton-seed cakes, have been fully examined, both as regards their composition and digestibility, but recently others have been introduced, earth-nut, decorticated cotton, cocoa-nut, sunflower-seed, &c., which have not been so experimented on until the authors of the present paper undertook the task.

The animals selected to test the digestibility of the cakes were two well-grown three-year-old sheep, which, previous to the commencement of the experiments, were well fed on second-crop hay, which was continued during the whole time of the experiments as the leading article of their diet, the cakes being added as a supplementary food. The experiments lasted from the beginning of December to the end of April, and were divided into nine terms, during each of which 250 grams of one description of cake was given with 750 grams of hay; in the cases of sunflower and sesame, 500 grams were given during portions of the time.

The quantities of each ingredient of the food daily eaten and voided in their excrement, solid and fluid, was carefully computed, and the increase of weight compared. In the course of the experiments, one of the sheep became ill and was replaced by another, with every precaution to prevent the results being vitiated.

Earth-nut cake was found to be easiest of digestion, and nearly the richest in nitrogenous matter of any of the cakes experimented with. It is recommended as a very strong and stimulating fodder, and is becoming a favourite with farmers, but would be more used were it not for irregularity in the quality. Much of the article as sold contains a quantity of black hairs, and some of the importations are damaged in the sea voyage, incipient decomposition setting in. The best cakes should be white, or of a clear reddish or yellowish tint. Decorticated cotton-seed, sesame, and sunflower seed-cakes are very much alike in composition and digestibility as fodder; they rank about the same in value. Cocoa-nut cake is an excellent and very tasteful fodder. Its composition very much resembles that of palm-nut cake; it should have ranked higher in value than the table shows, but the large proportion of fat is supposed to have disturbed the results. The composition of the oil-cakes used in the experiments was as follows (the air-dried samples):—

	Water.	Protein matter.	Fat.	Indi- gestible fibre.	Non-nitro- genous extract.	Ash and sand.
Earth-nut cake....	10.59	52.71	10.89	6.14	25.92	4.34
Cocoa-nut cake....	11.05	24.31	19.04	15.71	34.08	6.86
Cotton-seed cake ..	7.30	47.36	17.90	4.13	22.51	8.10
Sesame cake.....	12.75	49.09	11.48	7.07	21.32	11.04
Sunflower-seed cake	10.95	39.42	16.22	14.81	21.95	7.70



*Coefficients of Digestibility of the different Cakes and their Components.*

	Protein	Fat	Fibre	Non-nitro- genous extract	Organic matter	Relative nutritive value
	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.
Earth-nut cake....	47·89	9·33	0·97	24·07	82·26	1 : 1·00
Cocoa-nut cake....	18·39	18·95	9·66	26·29	73·29	1 : 4·47
Cotton-seed cake ..	40·11	15·68	—	18·85	74·64	1 : 1·42
Sesame cake .....	44·33	10·31	2·17	12·04	68·85	1 : 0·89
Sunflower-seed cake	35·31	14·24	4·51	15·56	69·62	1 : 1·55

J. F.

**Proportions of Nitrogen, Ash, and Phosphoric Acid in Successive Cuttings of Leguminous Fodder-plants.** By A. ROUSSILLE (*Ann. Agronomiques*, 7, 362—367). — It is well known that farmers give the preference to second cuttings as cattle food. On the other hand, Pierre has established that the nitrogen per cent. of dry matter decreases as the plants approach maturity. The first cutting, always consisting of more mature plants than the succeeding ones, the author has sought to determine experimentally whether the common agricultural practice is justified by Pierre's observation. The analyses were made on a mixture of lucerne with a little sainfoin, dried at 110—115°, and the results are contained in the annexed tables :—

	Stems.	Leaves and flower stalks.	Nitrogen p. c. of entire dry plant.	P <sub>2</sub> O <sub>5</sub> p. c.	P <sub>2</sub> O <sub>5</sub> ÷ N.
1st cutting ..	57·38	42·62	2·1541	0·26977	0·1250
2nd cutting ..	34·09	65·91	3·1361	0·33854	0·1078
3rd cutting ..	38·46	61·54	3·3138	0·42573	0·1284

The nitrogen, phosphoric acid, and ash were distributed in the stems and other portions as follows :—

		Nitrogen p. c. of dry matter.	P <sub>2</sub> O <sub>5</sub> .	Ash.
1st cutting	{ Stems .....	1·60	0·1749	4·32
	{ Leaves, &c. ..	2·90	0·3975	9·89
2nd cutting	{ Stems .....	1·93	0·1684	6·42
	{ Leaves, &c. ..	3·76	0·5025	11·63
3rd cutting	{ Stems .....	2·12	0·1834	8·53
	{ Leaves, &c. ..	4·06	0·5861	12·92

These analyses show that the second and third cuttings contain a much higher proportion of albuminoids and phosphates than the first cutting.

J. M. H. M.

**Cultivation of Lupines.** By MEIER (*Bied. Centr.*, 1882, 38—40). —The cultivation of lupines, and the employment of them as hay, is strongly recommended.

E. W. P.

**Report on Field and Feeding Experiments at Woburn, 1880.** By A. VOELCKER (*Ann. Agronomiques*, 7, 406—415; from *J. Roy. Agr.*

*Soc. England*, 1881, Part I, 112—132).—In this paper are detailed the results of the fourth year's experiments on the continuous growth of wheat and barley with natural and artificial manures, and on the relative value of dung from cotton cake and maize meal as manure for rotations.

J. M. H. M.

**Studies on the Decomposition of Orthoclase.** By J. STOKLASA (*Landw. Versuchs.-Stat.*, **27**, 197—207).—Notwithstanding many interesting observations on the weathering of felspar by Forchhammer, Bischof, and others, there remain many points in the process of kaolin formation which are as yet unexplained. The present paper is a contribution to a knowledge of the subject, being the result of examinations of 19 specimens of felspar from different sources and in various stages of decomposition, viz.: 1. Unweathered, yellowish-red, transparent. 2. Opaque, dull, with the upper surface partially decomposed. 3. Red, with strongly decomposed upper layers, the inner portion not attacked. 4. Specimens containing kernels of greatly decomposed matter. 5. Perfectly transformed kaolin. The process of decomposition is characterised by the gradual formation of silicates easily soluble in weak acids; the increase of alkalis principally soluble in concentrated hydrochloric acid, the diminution of density and increase of contained water, followed by solution of the silicates and formation of carbonates. Water containing carbonic anhydride in solution plays a very important part in the transformation of orthoclase into kaolin. Of three specimens (portions used in previous experiments and found insoluble in hydrochloric acid), 100 grams each were placed with a litre of water, saturated with carbonic anhydride, in well closed flasks and left undisturbed for three months, at the end of which time comparatively large quantities of matter had passed into solution; with the fully transformed kaolin, the case was different, traces only of alkalis passing into solution. The author thinks the process of decomposition is accompanied by an important molecular change in the constitution of the substance.

J. F.

**Phosphoric Acid in Volcanic Soils.** By L. RICCIARDI (*Compt. rend.*, **93**, 1514—1516).—A reply to some observations by P. de Gasparin.

C. H. B.

**Composition of "Reh," an Inflorescence on the Soil of Certain Districts of India.** By J. GIBSON (*Proc. Roy. Soc. Edin.*, **10**, 277—280).—This inflorescence, which is detrimental to the fertility of the soil, and seems to be increased in quantity by reason of the water in the high level canals forcing the subsoil salt-impregnated water to the surface of the neighbouring land, consists of  $H_2O$  2·5, insoluble inorganic residue 68·1, and 28·6 of matter soluble in water, of which the percentage composition is as follows:—

Na.	Fe.	$NH_3$ .	$SiO_2$ .	$SO_4$ .	$CO_2$ .	Cl.	Organic matter.	Mg.
32·4	0·5	1·2	1·2	41·3	12·3	8·8	2·4	trace.

All efforts to reclaim land infected with "reh" have hitherto proved abortive.

E. W. P.

**Ammonia-fixing Power of Certain Salts.** By MORGEN (*Landw. Versuchs.-Stat.*, 27, 183—195).—Farmers know that stable manure loses some of its most valuable ingredient—ammonia—by lying on the manure heap or in the stable, and that the loss is greater the longer it is so left; in order to avoid this, it has been the habit to strew the manure with certain salts which have the power of combining with the volatile ammonium carbonate or, as manure manufacturers describe it, of fixing the ammonia. Gypsum has generally been employed for the purpose, but lately the impure Stassfurt salts of potash have come into use, and these latter possess the advantage of enriching the manure with other valuable ingredients.

Hitherto no experiments have been recorded showing the suitability of different salts for this purpose, and the author proposes to partly supply the want by recording some made by him, with gypsum, kainite, magnesium sulphate, potassium sulphate, and magnesium chloride.

The experiments were intended to ascertain if the same quantity of fixing material will always combine with like quantities of ammonium carbonate, and if the composition of the different mixtures affects the results. Details are given of the *modus operandi*, and the results are carefully tabulated, and from the tables it is seen that the various substances vary considerably in their combining power, which is in great measure dependent on the amount of ammonia present. Potassium sulphate in all cases had the least effect; gypsum and sulphate of magnesium were the most regular in their operation; magnesium chloride coming next, and from its cheapness is recommended, the author having altered his opinion that injurious effects followed its use, referring to the recently published work of Maercker, *Potash Salts and their Employment in Agriculture*, to support his change of opinion. Further experiments were made as to whether the action of the substances employed was instantaneous or increased with time; the former was found to be the case.

The author's summary is that gypsum and magnesium chloride are the most desirable substances to employ in fixing ammonia, after which come magnesium sulphate and Stassfurt salts, kainite and kieserite when they can be obtained cheaply.

J. F.

**Value of Poudrette.** By F. SOXHLET (*Bied. Centr.*, 1882, 11).—The percentages of nitrogen and phosphoric acid in poudrettes from different towns are given, and the quantities vary from 3·5—0·74 per cent.  $P_2O_5$  and 9·96—6·02 per cent. N. The poudrette from Munich is very deficient in phosphates, which arises from the fact that the liquid is pumped out of the tanks, leaving a sediment which contains the greater part of the phosphates precipitated in consequence of the ammoniacal fermentation.

E. W. P.

**Preservation of Molasses Waste.** By E. ERNST-BEESENLAUBLINGEN (*Bied. Centr.*, 1882, 57).—To bring molasses waste into a useful form without loss of nitrogen, 100 parts of the waste are to be mixed with 15 parts dried peat and 20 parts sulphuric acid ( $66^\circ$ ), the mixture will contain about 3·5 per cent. N and 11 per cent.  $K_2O$ .

E. W. P.

**Falasco Manure from Sea-weed and Marsh-weeds.** By F. SESTINI (*Landw. Versuchs.-Stat.*, **27**, 176—182).—Sea-weed and wild plants from the saline marshes which border the Adriatic Sea, are much used in Italy for manure under the name of *Falasco*; mixed with stable manure and dug into the ground, the results are very favourable. The author has given a good deal of attention to the subject, and communicates the results of his observations. The plants used for making it are various, 14 species being enumerated, the greater number at the time of cutting being in the green state. Persons who wish to make the manure rent a plot of marsh and reap it, each "malter" (equal to 1.25 hectare), yielding from 11 to 14 kilos., costing generally 2.22 to 2.63 lire the centner.

The chemical analysis was made on carefully selected samples taken at different times during the mowing, and every precaution used; the samples are air-dried.

	Grams.
Water at 100° C. ....	14.94
Fatty matter extracted by ether.....	2.72
Cellulose.....	23.52
Protein matter .....	4.77
Hydrocarbons and non-nitrogenous matter (by difference) .....	49.37
Mineral matter—	
Ash freed from CO <sub>2</sub> .....	4.68
	<hr/>
	100.00

From analysis of the manure and of the residual ash, the author says that from 10 centners of the air-dried material costing, in the vicinity of Pisa, 22.20 lire, a farmer obtains 8.930 kilos. of nitrogen, 8.560 kilos. of potash, and 2.279 kilos. of phosphoric acid, besides appreciable quantities of other valuable materials. The *money value* of falasco, calculated at the lowest rates at which can be obtained (in Italy), nitrogen in stable manure, phosphoric acid in bones, potash from Stassfurt salts, is given as follows:—

100 kilos. Falasco contain—

	Lira.	Lire.
Nitrogen.....	0.893 at 1.00	0.89
Phosphoric anhydride ....	0.279 „ 0.35	0.10
Potash.....	0.856 „ 0.56	0.48
Sodium chloride.....	1.344 „ 0.12	0.16
Other matters.....	85.000 „ 0.03	0.85
		<hr/>
		2.48

but this does not allow anything for the valuable quality of the material for absorbing urine when used as bedding, which is very considerable. Compared with corn straw, falasco contains more carbonaceous and useful mineral matter, about the same amount of phosphates, nearly double the quantity of potash, and in addition a certain quantity of sodium chloride.

The experiments of Boussingault and Bechi show that 100 kilos. of the following substances, steeped 24 hours in water, absorb—

Grain straw.....	220 parts
Ferns.....	191 „
Chestnut leaves .....	150 „
Peat .....	198 „

The author making a similar experiment found the grain straw absorbed 280 parts of water, and the falasco 210 parts; it therefore is less useful an absorbent than straw in stables.

The use of salt is unknown as food for cattle over the district where falasco is used as manure; the author suggests experiments to ascertain the effects of manures containing salt on vetches and other field vegetables.

J. F.

**Aberdeenshire Experiments on the Relative Value of Soluble and Insoluble Phosphates.** By T. JAMIESON (*Ann. Agronomiques*, 7, 420—422).—In this note, the author replies to a criticism of Dr. Voelcker (*J. Roy. Agr. Soc. England*, 1880), on the Aberdeenshire Experiments of 1876—78.

The author maintains his opinion that the superiority of superphosphate to *finely ground* mineral phosphate on root crops is not so great as is generally supposed; he estimates it at 10 per cent. better, instead of being double the value.

J. M. H. M.

**Manuring Experiments with Superphosphates and Bone-meals of Various Degrees of Fineness.** By F. FARSKY (*Bied. Centr.*, 1882, 14).—In a previous communication (*Abstr.*, 1882, 90), it was shown that the value of superphosphates was, to a certain extent, dependent on the fineness of the grain; that coarse and fine grain both act better on clay than on lime soils, and that superphosphates should be placed at least 3 cm. below the surface so as to avoid reduction: for the roots to be benefitted a depth 6—20 cm. is best, and for the crops 6—12 cm. In other experiments, in which coarse-grained (0.25—0.75 cm.) and fine-grained (less than 0.25 cm.) steamed bone-meals were employed for beet, the same results were obtained as before, the coarser kind being the best.

E. W. P.

**Phosphatic Manures on Turnips; a Report of Experiments carried out in Scotland in 1880.** By G. BROWN (*Ann. Agronomiques*, 7, 416—420, from *Agricultural Gazette*, 1881).—The experiments were carried out simultaneously by farmers in five different localities. Duplicate plots of one-eighth or one-quarter of an acre received a good dressing of farmyard manure in the autumn, and the turnips were grown with the following quantities of artificial manures, arranged so as to contain equal amounts of phosphoric acid:—Bone-meal, 627 kilos. per hectare; dissolved bone, 893 kilos.; mixture of bone-meal and bone superphosphate, 760 kilos.; farmyard manure, 627 kilos.; ground coprolites, 627 kilos.; mineral superphosphate, 1025 kilos.; mixture of ground coprolites and superphosphate, 790 kilos.

Berwickshire (J. Wilson, Chapel Hill). Soil, stony, well drained

clay; turnips after oats, preceded by three years' pasture, fed off with sheep. All the phosphatic manures gave results superior to the farmyard manure alone; bone-meal alone, or mixed with superphosphate, gave the best yield, and at less expense than bone superphosphate.

Stirlingshire (J. Murray, Muniston). Clay soil, containing only traces of potash; carried turnips in 1873, then oats, followed by seeds. The best plot was that manured with mixed coprolites and mineral superphosphate; next came dissolved bones, and mineral superphosphate employed alone; last of all the artificial manures was the bone meal, which gave a yield very little better than farmyard manure alone.

Banff (J. Simpson, Clunnymore). Clay soil, containing 0.05 per cent.  $P_2O_5$ : cropped for the last 40 years on the following quinquennial rotation:—(1) oats with rye-grass and clover; (2) and (3) rye-grass and clover; (4) oats; (5) turnips. The two best plots were those carrying bone superphosphate and bone-meal. Another series of experiments in which no farmyard manure was employed showed little or no benefit from the employment of phosphatic manures.

Caithness (J. Logan, Ulbster). Stony soil, cropped according to the quinquennial rotation, and under oats in 1879. All the phosphatic manures showed better results than farmyard manure alone. Bone-meal and ground coprolites gave the best yield with least expense.

Caithness (G. Brown, Watten Mains). Clay soil, an old red sandstone, very favourable to growth of roots; six years' pasture and a crop of oats preceded the turnips. On the plots which had received farmyard manure, bone superphosphate gave the best result; on the plots without farmyard manure, the mixture of ground coprolites and superphosphate gave almost as good a result as dissolved bones, both manures doubling the crop as compared with the unmanured plots.

The author thinks that the superiority of bone-meal or coprolite to superphosphate shown in seven of the experiments, is perhaps exceptional, and may be due to the exceptional dryness of the season from August 5 to September 10, 1880. J. M. H. M.

**Manuring Experiments on Barren Sandy Heath.** By A. MAYER and others (*Bied. Centr.*, 1882, 82—84).—A soil which was quite barren was caused to produce fair crops by the employment of bone-meal, potassium chloride, and peat, having first been green-manured with lupines. The best results were obtained with a mixture of all three manures, the unmanured plot producing only 1.2 kilo. rye-grain per hectare, whilst the manured plot produced 472. In the succeeding year, the same manures were employed with addition of ammonium sulphate, and, in some cases, of slaked lime; the best crop of potatoes was that yielded by the mixture of the four, without lime. The value of the crop more than repaid the expenses, so that it is evident that the addition of peat soil is productive of lasting benefit, not only as giving nourishment, but as effecting an alteration in the physical character of the land. E. W. P.

**Manuring of Sugar-beet.** By M. MÄRCKER (*Bied. Centr.*, 1882, 15—18).—The first set of experiments showed that as regards yield and

quality it was advantageous to employ highly concentrated in place of ordinary supers. There is no advantage in manuring beet with nitrate of soda in the autumn instead of in the spring, and ammonium sulphate manurings lag behind nitrates; but if the sulphate is added during autumn, there appears to be a gain; it is not greater, however, than with the crop from nitrates.

A mixture of potassium sodium nitrates was compared with ordinary sodium nitrate, and the manures were applied in autumn and in spring, but no appreciable difference could be noticed; the mixed nitrate did not appear to be superior to the sodium salt, nor was any difference noticed in the quality of the roots. It is well known that sugar-beet when kept loses sugar, and this loss is greatest when nitrogen has not been used as a manure.

E. W. P.

**Alteration in the Composition of Irrigating Water and its Action.** By J. KÖNIG and C. KRAUCH (*Bied. Centr.*, 1882, 73—79).—The greatest amount of water is absorbed by the soil during autumn (30 per cent.) by reason of the dryness of the soil which requires a larger amount of water to saturate it; whilst in spring time, the soil being nearly saturated, a much less quantity is required. When soil was placed in boxes and then irrigated, only about 7—8 per cent. was retained, and the water only penetrated to a depth of  $\frac{1}{3}$  m. during continuous heavy rain; whereas under natural conditions the rain attained a greater depth, because of passages formed in the earth by moles, &c. Drains generally begin to run after the rain has ceased falling, and, as part of the water passes through the passages above mentioned, it soon assumes the temperature of the surface-water, while that of the soil is but slowly altered. In flowing over meadows, the temperature of the water rapidly approaches that of the air; yet in cold weather it is always warmer than the air, so keeping the soil warm. It appears that the soluble mineral matter in the water is removed to a greater extent during warm weather, and that the plants absorb their mineral food directly from the water as they require it, and that but a very small proportion of soluble matter is absorbed by the soil itself. An exception to this is found in the case of potash, which seems to be the only substance really removed from the water by the soil, and retained; these conclusions are drawn from the observations made that at all times of the year the drainage-water is poorer in potash than the water which flows on to the surface, and that it is only during the period of vegetation that the other matters are absorbed.

Application of manure to the soil has a considerable influence on the composition of the water, whether flowing off the surface, or through the earth as drainage. Potash causes an elimination of lime from the soil, and 65 per cent. of the phosphoric acid applied in the irrigating water is retained. The experiments with the soil in boxes only show a retention to the amount of 21 per cent.; under artificial circumstances 16.2 per cent. of the ammonia is retained.

The water flowing off the surface of the meadow shows an increase in organic matter, whilst in the drainage there is a reduction; the drainage water, on the contrary, contains less oxygen and more

carbonic anhydride than the surface water. The result then of irrigation is to cleanse the soil of an excessive quantity of organic matter, and to remove "sourness;" the water is not fit for further irrigation until, by exposure to the air, it is thoroughly oxygenated, and the excess of carbonic anhydride is given off to the air. E. W. P.

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## Analytical Chemistry.

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**Action of the Electromagnet on Various Minerals, and its Use for their Mechanical Separation.** By C. DOELTER (*Monatsh. Chem.*, 3, 139—163).—Ferruginous minerals subjected in the state of powder to the action of an electro-magnet are attracted in various but determinable degrees, according to the proportion of iron contained in them and the state in which it is present; and this action may be utilised for separating them from non-ferruginous minerals and from each other, when they occur together in ores or rocks.

I. To determine the relative intensities with which a number of minerals are attracted, it is necessary to subject them all to the action of the same electromagnetic force. For this purpose the author used an electromagnet consisting of a long straight iron bar enclosed in a wooden cylinder wound round with copper wire. The pulverised minerals placed in watch-glasses were brought to the lower end of the bar, which had an ellipsoidal termination, and moved about so as to bring all the particles of the powder successively in contact with the magnetic pole. The quantities of the several minerals thus taken up by the magnet in equal times, without interruption of the current, were regarded as measures of the relative forces with which they were attracted.

The action of the electromagnet was tried in this way with currents of various strengths produced by two to ten Bunsen's cells. It was not found advantageous to use more than twelve, partly on account of the heating of the wire, partly because the further addition to the number of cells did not produce any perceptible increase in the magnetic movement at the end of the bar.

Another mode of experimenting consisted in measuring the relative distances at which the particles of different ferruginous minerals began to be attracted by a powerful electromagnet, excited by 10—12 cells; but this method was not found to give results equal in accuracy to those obtained by weighing the quantities of the powders taken up by actual contact with the magnetic pole.

The general results of the experiments are as follows:—The relative attractive forces exerted on the several minerals depend, not on the absolute quantity of the iron, and not always on the amount of ferric or ferrous oxide in the compound. The greatest capacity of attraction is exhibited by the oxides hæmatite and ilmenite. Next in order come ferrous carbonate, almandin, lievrite (with  $20\text{Fe}_2\text{O}_3$  and  $35\text{FeO}$ ), hedenbergite with  $27\text{FeO}$ , iron magnesium carbonate, ankerite with

20FeO, to which limonite is nearly equal. Next to these come the highly ferruginous augites and hornblendes, arfvedsonite ( $26\text{Fe}_2\text{O}_3$ ), augite from Pico da Cruz ( $17\text{FeO}$ ), epidote ( $15\text{Fe}_2\text{O}_3$ ), augite from Vesuvius ( $10\text{FeO}, \text{Fe}_2\text{O}_3$ ), pyrope and tourmalin ( $9\text{FeO}$ ); then the less ferruginous augites and hornblendes; the olivins, excepting those which contain large proportions of iron (as that of Pico da Cruz), which ranks near epidote; then the highly ferruginous sulphides, which, in spite of their large proportion of iron, exhibit very little attractivity; also vivianite containing 45 per cent. iron oxides, and ferrous sulphate. At the end of the series come mica, chlorites and silicates very poor in iron, such as diopside, hauyn, and those which contain very minute enclosures of iron-minerals, such as nephelin and leucite.

In the following series the more important minerals are arranged in the order of their attractivity, those which exhibit but slight differences being placed in the same horizontal line:—

Magnetite,  
 Hæmatite, Ilmenite,  
 Chromite, Siderite, Almandin,  
 Lievrite, Hedenbergite, Ankerite, Limonite,  
 Iron-augite,\* Pleonast, Arfvedsonite,  
 Hornblende, light-coloured Augites, Epidote, Pyrope,  
 Tourmalin, Bronzite, Idocrase,  
 Staurolite, Actinolite,  
 Olivin, Iron Pyrites, Copper Pyrites,† Vivianite, Ferrous  
 Sulphate,  
 Tetradymite, Bornite, Zinc-blende,‡ Biotite, Chlorite, Rutile,  
 Hauyn, Diopside, Muscovite,§  
 Nephelin, Leucite, Dolomite.

II. *Application of the Electromagnet to the Mechanical Separation of Minerals.*—For this purpose, the author uses a horse-shoe electromagnet, which, with a small number of voltaic cells, exerts a stronger attractive power than the apparatus above described. A mineral theoretically free from iron, such as felspar, leucite, or nephelin, may be easily separated from admixed ferruginous minerals by subjecting the mixture in the state of fine powder to the action of the electromagnet excited by a moderately strong current, from six to eight couples. For isolating ferruginous minerals, on the other hand, it is better to use a weaker current, in order to avoid the possibility of minerals containing enclosures of iron-compounds being attracted at the same time; it is better also not to pulverise the mixture too finely.

For separating and purifying the constituents of rocks in petrographic investigations, the electromagnetic method may also render

\* Containing 15 to 20 per cent. iron oxides.

† Many varieties of copper pyrites are very powerfully attracted, even by a strong magnetic needle; such varieties probably contain magnetite.

‡ Dark-brown, ferruginous: the light varieties rank with nephelin.

§ Micas are very difficult to arrange, as it is not easy to obtain them in grains of uniform size: very finely pulverised biotite is about as magnetic as actinolite.

good service; instead of, or as supplementary to, the method of separation by means of mercuric iodide.

For example, a *nephelin-syenite*, from the island of Antao, consisting of augite, hornblende, magnetite, orthoclase, plagioclase, and nephelin, was decomposed as follows:—The magnetite was first removed by the magnet, then the augite and hornblende, while the nephelin and felspar remained behind. The nephelin was then extracted by means of a stronger current, but the separation thereby obtained was not complete, so that it had to be supplemented by treatment with dilute acids. In this way the rock was found to consist of 5 per cent. magnetite, 30 augite and hornblende, 10 nephelin, 35 felspar, and 20 products intermediate between nephelin and felspar.

A *phonolite* from Praga, consisting of orthoclase, nephelin, augite, and magnetite, was first freed from magnetite, and then, by means of the strong apparatus, a mixture of augite and nephelin was extracted from it, which was decomposed by solution of mercuric iodide. The composition of the rock was thus found to be:—

Magnetite .....	4.0 p. c.	Mixture of felspar (pre-dominant) with nephelin).....	11.0 p. c.
Augite .....	11.0 „		
Nephelin .....	48.5 „		
Orthoclase .....	25.5 „		
			<hr/> 100.0 „

Several other examples are given in the paper.

In the decomposition of rocks, it is of great advantage to be able to vary the attractive power of the electromagnet; and for this purpose it is desirable to have at disposal two electromagnets, one very strong and excited by two to four couples, being used at varying distances of the powder from the poles, whilst the weaker one is employed for direct contact of the powder with the poles, the strength of the current being varied (two to ten pairs). Beginning with the former, the oxides and highly ferruginous silicates, augite, epidote, &c., may be removed, leaving behind the olivin, biotite, slightly ferruginous augites and hornblendes. The remaining minerals, which do not differ from one another so greatly in their attractivity, may be better separated with a weaker apparatus, the powder being in direct contact with the poles, and the strength of the current being varied. H. W.

**Separation and Determination of Potash and Soda by the Indirect Method in Plant-ashes, Fertilisers, and similar Substances.** By C. RICHARDSON (*Amer. Chem. J.*, 3, 422—424).—The indirect method of estimation is capable of giving good results with mixtures of the pure chlorides of potassium and sodium; but on attempting to apply it to the estimation of the alkalis in plant-ashes, the usual method of separating the mixed chlorides does not yield them in a state of purity sufficient for the accuracy which this mode of estimation requires. The following method yields these chlorides perfectly pure:—

The impurities which are usually met with and resist removal are

phosphoric acid and magnesia, and to remove the latter completely it is first necessary to get rid of all strong acids. For this purpose, the ash is dissolved in nitric acid, and the liquid evaporated, this treatment being repeated several times to ensure the conversion of the chlorides into nitrates. The residue is then taken up with water; a few grams of oxalic acid are added; and the solution is again evaporated once or twice on the steam-bath. The nitrates are then converted into oxalates, and on gentle ignition into carbonates. The residue, containing only phosphates, sulphates, and carbonates, is then dissolved in water, the solution filtered through a small filter, and the filtrate, thus freed from the greater part of the lime and magnesia as phosphates, sulphates, and carbonates, is boiled with a slight excess of barium hydrate, and again filtered, whereupon there remain in solution nothing but the alkalis and the excess of baryta. To ensure complete freedom from magnesia, however, the filtrate is evaporated to dryness, much of the baryta, as well as the alkalis, being at the same time converted into carbonates.

The residue is then treated with successive portions of water, not more than 5 c.c. at a time, and passed through a filter 7 cm. in diameter; the filtrate is treated with ammonium carbonate as free as possible from empyreumatic matter; and after evaporation to dryness, the residue is again taken up with water, and the solution passed through a small filter into a weighed platinum dish. This is to be covered with a watch-glass; pure hydrochloric acid added; the solution evaporated; the residue gently ignited, and redissolved in water; the solution filtered to remove a small amount of black carbonaceous matter; again evaporated; and the residue heated to  $130^{\circ}$  and weighed. The chlorides are thus obtained quite pure and white, and ready for the determination of chlorine.

This method yields very exact results. The usual method with platinum has a tendency to throw all the error into an exaggeration of the amount of sodium present, especially if the mixed chlorides are impure; and in this way many of the older analyses show a percentage of sodium in the ashes of plants which, when analysed according to the more exact method described, are found to be free from that element.

H. W.

**Action of Acetic Acid on Dolomite.** By HAUSHOFER (*Jahrb. f. Min.*, 1882, 1, Ref., 361).—The constituents of dolomite are dissolved in considerable quantity by dilute acetic acid, even at low temperatures, so that this acid cannot be used for separating dolomite from calcite. The quantity of matter dissolved increases with the temperature, and with the duration of the action; it is for the most part greater with comparatively dilute acid (12 per cent.) than with stronger acid (50 per cent. pure acetic acid). Citric acid acts much more strongly than acetic acid.

In dolomites whose composition is very nearly represented by the formula  $\text{CaCO}_3, \text{MgCO}_3$ , the composition of the residue approximates much more nearly to normal dolomite than that of the dissolved portion, which indeed contains a larger proportion of magnesia than either the original dolomite or the residue. In normal dolomites,

therefore, the magnesia dissolves more readily than the lime. Highly calciferous dolomites on the other hand yield a solution much richer in lime and a residue much richer in magnesia than the original dolomite. In no case was a residue obtained having the composition of normal dolomite. The author regards the difference in composition of the dissolved and residual portions as the result of fractional solution, and infers from this fact that dolomite is not a homogeneous chemical compound, that is to say, a double carbonate of calcium and magnesium, but rather that all dolomites are isomorphous mixtures of the normal carbonates of calcium and magnesium.

H. W.

**Action of Mercuric Chloride on Cast Iron.** By G. ZABUDSKY (*Jour. Russ. Chem. Soc.*, 1882, 111—113). According to Boussingault, on decomposing carbide of iron (in steel, cast iron, &c.) by mercuric chloride, the combined carbon separates out in the free state, and pure carbon remains behind, if the mercury and mercurous chloride are removed by distillation in a current of dry hydrogen. The residue consists, however, as the author has shown, not of pure carbon, but of a compound, containing carbon, hydrogen, and oxygen. For this purpose the mercury and mercurous chloride were removed either by water and a current of chlorine, or the mercurous chloride by a solution of sodium sulphate. In the first case a chlorine compound remained behind, in the second a compound containing  $C = 68.93$ ,  $H = 3.70$ .

On distilling the latter compound in a current of dry hydrogen, a black body remains behind, containing  $C = 96.50$ ,  $H = 2.42$ , so that, from the quantity of carbonic acid weighed (according to Boussingault's method), instead of 4.10 per cent., only 3.54—3.62 per cent. of carbon is found, this being due to a loss of carbon in distillation.

B. B.

**Electrolytic Determination of Copper.** By J. B. MACKINTOSH (*Chem. News*, 45, 101).—The author has made a series of experiments with the Luckow electrolytic determination of copper. The alloy was dissolved in nitric acid, the solution evaporated to dryness, the residue dissolved in water with addition of a few drops of nitric acid, and to this solution four or five drops of a concentrated solution of citric acid was added. This solution was then precipitated in a platinum dish with a current from two Bunsen cells of about one quart capacity. The deposited copper was analysed, and the carbon, hydrogen, and nitrogen in it determined, and it is concluded that some organic matters, and most probably all, in the presence of nitric acid in the copper solution undergoing electrolysis, cause erroneous results; that from a nitric acid solution, with no organic matter, it is extremely difficult to separate all the copper; and that the old method of electrolysis from the sulphate is the best.

Luckow replies, stating that he added tartaric acid to the nitric solution of copper only with the special purpose of preventing the injurious action of manganese salts, when present, with special reference to the assay of the Mansfeld copper shales. He states also that the form of the apparatus was designed with that special object.

D. B.

**Volumetric Estimation of Antimony in Presence of Tin.**

By E. F. HERROUN (*Chem. News*, **45**, 101).—The process depends on the fact that antimonious chloride is reduced to antimonious chloride by hydriodic acid, with liberation of iodine, whilst stannic chloride is not reduced. The free iodine is estimated by means of a standard solution of sodium thiosulphate. Since 122 parts of antimony liberate 254 parts of iodine, the amount of iodine found multiplied by 0.48031 will give the amount of antimony present. If iron or other metal, whose perchloride is capable of liberating iodine, is present in the alloy, the tin and antimony may be obtained as oxides by treating the alloy with nitric acid and evaporating, and after being well washed, may be boiled in strong hydrochloric acid, and the antimony determined as indicated. D. B.

**Plastering of Wine.** By E. REICHARDT (*Arch. Pharm.* [3], **19**, 433—441).—The author points out that when a must is treated with gypsum, potassium sulphate goes into solution with tartaric acid, and that calcium tartrate is left undissolved. He has shown that gypsum itself is practically insoluble in wine.

It is assumed that the ash of non-plastered wines should be alkaline, and should evolve carbonic anhydride on treatment with acids. Marty has found 0.194—0.583 per cent. of potassium sulphate in natural wines. The author seems to consider that 0.2 per cent., or somewhat more, of potassium sulphate, should be taken as the limit in the examination of wines. F. L. T.

**Examination of Milk.** By L. JANKE (*Chem. Centr.*, 1882, 13—16 and 27—32).—1. *Determination of the Solid Matter in Milk.*—(a.) With addition of sand: 10 grams of milk and 20 grams of perfectly dry sea-sand are accurately weighed into a tared basin of about 50 c.c. capacity, and evaporated on the water-bath. The basin and contents are then dried at 100° until the weight is constant. When perfectly cold, the basin with contents is weighed in a desiccator over sulphuric acid. (b.) Without sand. To check the preceding determination, 10 grams of milk are evaporated in a Hofmeister capsule without the addition of sand. Both methods give results agreeing closely with one another. Fifty determinations were made with sea-sand and an equal number without sand, the greatest difference amounting to  $\pm 0.14$  per cent., and the smallest difference being  $\pm 0.01$  per cent. The sp. gr. of the fifty samples is also given, the lowest number being 1.0261, the highest 1.0335, and as a mean 1.0309.

The author wholly disregards the sp. gr. in judging of the purity of milk, and objects to the assertions of Sell, Kirchener, Soxhlet, Klenze, Vicht, Orth, Wittmack, and others, who consider milk to be adulterated when its limits of sp. gr. are outside 1.029—1.033. Gerber and Radenhausen mention that the determination of the total solid residue by evaporating milk after coagulation with alcohol or acetic acid, gives more accurate results than the method of drying with sea-sand. This the author disputes.

2. *Determination of Fat in Milk.*—(a.) From the dry substance without the use of sea-sand. The residue in Hofmeister's capsule is

ground to a fine powder and wrapped up in a filter, and the fat extracted with ether in Soxhlet's apparatus (described *Dingl. polyt. J.*, 1879, 232). (b.) From the dry substance with the use of sea-sand. The residue is ground to a fine powder and mixed intimately with perfectly dry marble. The mixture is transferred to a glass tube, 1.8 cm. wide and 60 cm. long, drawn out to a fine point at the lower end, and provided with a plug of cotton-wool, and the fat is extracted with ether.

The author has made a large number of fat determinations by Soxhlet's method, and concludes that the results are as trustworthy as those obtained by the ordinary gravimetric method. D. B.

**Composition, Properties, and Analysis of Milk.** By FLEISCHMANN and others (*Bied. Centr.*, 1882, 131—134).—From observations lasting over three years, Fleischmann considers that in morning milk the fat, dry matter, and sp. gr. are lower than in evening milk. The difference is but slight yet constant. Cameron and Chesnel have come to the same conclusions. Fleischmann communicates analyses of ewe's milk. Arnold states that unboiled milk colours guaiacum tincture blue, boiled milk does not, also that unboiled milk rapidly blues potassium iodide and starch; boiled milk but slowly. If milk, after standing 12—20 hours, be coagulated with acetic acid, and the whey mixed with potash and copper sulphate, it will give the characteristic violet coloration for peptones, which seem to be gradually formed in the milk, as fresh milk when coagulated does not exhibit this reaction. G. Marpmann recommends in the analysis of milk that the drying in a basin with sand, &c., be dispensed with, but that cotton-wool should be moistened with the liquid, and then dried in a tube by passing hot air through: the fat may then be removed from the cotton by benzene. Mittelstrasse's milk tester is compared by Veith with Soxhlet's apparatus, and with the gravimetrical process. The errors are somewhat large, far larger than those of Soxhlet's.

F. Farsky has made a large number of experiments on the effect produced on creaming by salicylic acid. Creaming in open vessels is more regular and slower than in closed vessels; souring occurs sooner in the latter: creaming takes place quicker in shallow and broad vessels than in those that are deep and narrow. The milk also turns sour sooner in the deep than in the shallow vessels; the larger the surface of the milk, and the lower that surface is below the rim of the pans, so much the more slowly does souring occur. Creaming occurs quicker at the higher temperatures, but the cream is less in quantity, and becomes sour sooner. The addition of water containing salicylic acid causes the milk to cream more quickly; the more acid added, the longer is the time required for coagulation; the acid, 0.3—0.5 gram per litre, should be poured carefully on to the surface and not stirred.

E. W. P.

**Test for Distinguishing Cotton-seed Oil from Olive-oil.** By M. ZECCHINI (*Gazzetta*, 1882, 61).—The author recommends for this purpose pure colourless nitric acid, free from nitrous products, and having a density of 1.40. Acid of this strength forms with pure olive-oil at first a colourless or slightly straw-coloured mixture, changing to

light dove-grey with yellowish reflex, whereas with cotton-seed oil it forms at first a golden-yellow mixture, afterwards changing to a coffee-brown colour so deep as to be almost black. To apply the test, the two liquids are mixed in a test-tube closed with a caoutchouc stopper, and shaken together briskly for about half a minute, the tube being then left to rest in a vertical position for five or six minutes. This method serves for the detection of 0.5 per cent. cotton-seed oil in olive-oil. It is essential to use acid of the strength above mentioned, for weaker acid, *e.g.*, of sp. gr. 1.22 to 1.33, produces with cotton-seed oil only a light-coloured liquid, scarcely distinguishable from that formed with olive-oil; while on the other hand, strong acid having a sp. gr. of 1.40 and charged with nitrous products, gives a dark colour even with pure olive-oil.

H. W.

**Quantitative Separation of Rosin from Fats.** By T. T. GLADDING (*Amer. Chem. J.*, 3, 416—419).—The author's method is similar to that which is adapted for the separation of oleic acid from stearic and palmitic acids by the different solubilities of their lead salts in ether, and consists in treating the alcoholic solution of the resinous and fatty acids with neutral silver nitrate, which throws down the fatty acids as silver salts, leaving the silver resinate in solution. The precipitate having settled down, the clear liquid is mixed with ether and shaken up with dilute hydrochloric acid till the dissolved silver salt is completely decomposed; and after all the resulting silver chloride has subsided, the ethereal solution is syphoned off and evaporated to dryness over a water-bath. The residue consists of rosin containing a small quantity of oleic acid, which can be accurately allowed for. The chief use of the process is for the estimation of rosin in soap, to which it may be applied directly without previous decomposition of the soap by acids. Its success, however, requires attention to a number of details, for which the original paper must be consulted.

H. W.

**Gelatin Jelly as a Dialyser.** By R. C. WOODCOCK (*Chem. News*, 45, 79).—The author mentions that Dupré employs jelly prepared from gelatin for the separation of artificial colouring matters in wines, but its application to ordinary analysis has never been carried out. Its use in toxicological chemistry demands attention, and the author has devoted some time to the subject. He mixed soup extract with various quantities of strychnine, added jelly prepared from gelatin, and dialysed the mixture for 60 hours. The liquor was poured off, and the mass was well washed and heated in a beaker in a water-bath, until a film of gelatin formed on the surface. It was cooled, treated with alcohol, which precipitated a large proportion of the gelatin, and ether was added to complete the precipitation. The mixture was well stirred, when the gelatin adhered in a mass, so that the liquor poured off sufficiently clear without filtration. It was evaporated to dryness, and the residue moistened with concentrated sulphuric acid, which was kept at 60° for eight hours, when water was added, and the mass filtered from a slight charred residue. The filtrate was made alkaline with ammonia and extracted with chloroform. The extract was evaporated,

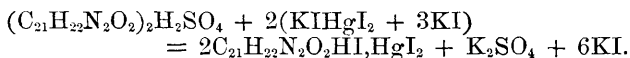


treated with a few drops of concentrated sulphuric acid, and tested for strychnine with potassium dichromate. The reaction was distinct. The author is continuing his investigation with other alkaloids, metallic substances, &c. Further experiments may prove that the time for dialysing can be considerably shortened. D. B.

**Estimation of Alkaloids by Potassiomeric Iodide.** By A. B. PRESCOTT (*Chem. News*, 45, 114—115).—For the volumetric determination of the chief natural alkaloids, Mayer (*ibid.*, 7, 159, and 8, 117, 189) proposes the use of a standard solution of mercuric iodide with excess of potassium iodide. The standard solution was decinormal, generally known as Mayer's solution. Mayer so far extended his investigation that for twelve alkaloids he stated the number of milligrams of alkaloid precipitated by a cubic centimeter of his standard solution. The general correctness of these volumetric factors declared by Mayer has obtained frequent confirmation, although some of his numbers have been found to require adjustment; moreover, it has been found that the proportion of alkaloid to iodo-mercurate is in many cases varied by the conditions under which the precipitation takes place, so that limits of dilution, time, temperature, &c., need to be prescribed. As a working process there still lacks an indicator for the end of the reaction. Another demand for more investigation of the subject lies in apparent discrepancies between the volumetric factors of precipitation and some gravimetric analyses of the precipitates. At various times the author has obtained some work on several of these questions, reaching, as yet, few conclusive results, but which he thinks may serve to put this subject and its deficiencies in a more tangible shape.

A few years before Mayer's report, T. B. Groves made some investigations on compounds of mercuric iodide and bromide with the alkaloids. Precipitates were prepared from solutions of "one equivalent of alkaloid" in salt, and with some excess of mineral acid; and "three equivalents of iodide (bromide) of potassium" with "one equivalent of mercuric chloride," and quantitative determinations made of the mercury and the iodine in these precipitates. In these analyses a dried and weighed portion of the (washed) precipitate was dissolved in boiling alcohol, and the solution treated with excess of fresh ammonium sulphide to precipitate the mercury; the solution was kept hot, slightly acidulated with nitric acid, and the mercuric sulphide separated and weighed. The filtrate was warmed and treated with silver nitrate for the gravimetric determination of the iodine. The difference was estimated as alkaloid. Analyses of the morphine, strychnine, quinine, and cinchonine compounds were made. The results are given in support of the general formula (translating  $\text{Hg} = 100$ )  $\text{RHgI}_3$ . This would be generally referred to the rational form  $\text{RHI}, \text{HgI}_2$ . However, the formula is not very well supported by the results. Groves remarks that the percentages of quinine and cinchonine obtained correspond with molecular weights one-fourth less than those received. The author recently obtained some determinations by Judson and Payne of the percentages of iodine and mercury in the iodo-mercurates of several alkaloids. The alkaloid precipitate

was dried at  $100^{\circ}$ , and a weighed portion dissolved in hot alcohol. It was found that the strychnine precipitate could be dissolved by acidulating the hot alcohol with sulphuric acid. The iodine was then precipitated with silver nitrate, and the filtrate treated with hydrochloric acid, filtered, and the solution charged with washed sulphuretted hydrogen gas. The resulting mercuric sulphide was washed, dried at  $100^{\circ}$ , and weighed. Having the iodine and the mercury, the fraction of hydrogen for the  $\text{HI}$  of the assumed formula was added, and the difference placed as alkaloid. The results of the analysis of the strychnine precipitate in absence of direct determinations of the alkaloid raise the question whether the iodomercurate of strychnine as a precipitate may not be in some degree complex and variable. This precipitate is one of the least soluble of the iodomercurates; according to Mayer being obtained in a solution containing  $\frac{1}{150000}$  of strychnine. The end of the reaction is distinct, and the precipitate settles fairly in acidulated water, but better in a concentrated solution of potassium chloride. In this solution, Dragendorff found each cubic centimeter to dissolve 0.00216 g. of the precipitate. Without potassium chloride, 0.1127 g. of strychnine lost 0.0021 g. in precipitating and washing; these gravimetric experiments indicate that the precipitate in question consists, mainly or wholly, of a double iodide of the formula  $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2\text{HI}, \text{HgI}_2$ . The volumetric factor of 0.0167 g. strychnine ( $\frac{1}{20000}$  of  $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2$  in grams) for 1 c.c. Mayer's solution (containing  $\frac{1}{20000}$  of  $\text{HgI}_2 + 4\text{KI}$  in grams) is well established. As we have little knowledge of the chemical composition of potassium mercuric iodide, our understanding of the chemical equation in the formation of these alkaloid iodomercurates must depend on the composition of the precipitate. As a suggestion, the following equation may be taken:—



This presupposes the following formation of Mayer's solution:  $\text{HgCl}_2 + 6\text{KI} = \text{KI}, \text{HgI}_2 + 3\text{KI} + 2\text{KCl}$ . The conditions of mixture of Mayer's solution seem to deny that it holds 3 mols. of free potassium iodide. Nevertheless, some experiments in support of the above equation are cited.

D. B.

**Method for Estimating the Total Alkaloids in Barks.** By J. DE VRIJ (*Pharm. J. Trans.* [3], 12, 765).—This is a modification of the method proposed by Proliis (*Arch. Pharm.*, 1881). 10 grams of the finely powdered barks are shaken at intervals during an hour with 200 grams of a mixture of 88 per cent. ether, 8 per cent. alcohol (92—95 per cent.), and 4 per cent. ammonia solution. At the end of the hour any loss due to evaporation of the ether is made up. A weighed quantity of the clear solution is freed from ether by distillation; the residue transferred to a weighed porcelain dish and dried over a water-bath; and the weight of alkaloid and waxy matter determined.

To estimate the pure alkaloid, the crude residue is treated with dilute hydrochloric acid, filtered, and washed until the washings give

no precipitate with soda. The filtrate is then made alkaline and shaken with chloroform. The chloroform solution is distilled, and the residue transferred to a weighed basin and stirrer, and heated over a water-bath until the weight is constant. L. T. O'S.

**Opium Assay.** By E. R. SQUIBB (*Pharm. J. Trans.* [3], 12, 724—726).—The author modifies Flückiger's process as follows:—In selecting the sample, which is of much importance if the opium is to be assayed for morphine, every tenth lump in the case is selected, and a cone-shaped piece cut out of the middle of each; then from the side of each cone a thin strip is cut from the apex to the base. These strips are then worked into a homogeneous lump, whilst the cones are returned to their places in the respective lumps. Three portions of the sample of 10 grams each are weighed whilst moist, and in one the moisture is determined by drying at 100°. Another is used for the immediate assay, whilst the third is reserved for a check assay.

The weighed portion is put into a tared flask, treated with 100 c.c. water, well shaken, and allowed to digest over night or for 12 hours, with occasional shaking. If the shaking be frequent and active, the time of digestion may be shortened to 3 hours. After digestion, the whole mixture is thrown on a filter. Some opiums give rise to magmas, which will not filter; in such cases the opium is washed with 30 c.c. ether and filtered, and finally washed with 20 and 10 c.c. ether. The residue is then dried and used, as in the case of opium not requiring previous washing with ether. Opium which has been adulterated or standardised with dextrin, sugar, or glucosides, must be exhausted with alcohol previous to treatment with water. For this purpose a mixture of equal volumes of alcohol and water (sp. gr. 0.820) may be used if the sample is not much adulterated; but generally a mixture of alcohol and water in the proportion of two to one is to be preferred. For the exhaustion and washing, 200 c.c. should be used. The process, after exhaustion, is the same as when water alone is used as the solvent.

The filtrate from the digestion with water is collected in a tared or graduated flask, and washed with water until the filtrate measures 120 c.c.; this is set aside. The residue is then transferred to a flask, shaken with 30 c.c. water, and again filtered and washed until the filtrate contains 70 c.c. In cases of opium rich in morphine, further exhaustion is necessary, the latter operation being repeated. The residue is dried at 100° and weighed.

The washings are evaporated in a tared basin at 90°, and, when they have been reduced to a small bulk, the 120 c.c. of the first filtrate is added, and the whole reduced to about 20 grams. After cooling, 5 c.c. of alcohol are added, and the solution well stirred. Any precipitate that may form is filtered off, washed, and the filtrate evaporated to 25—30 grams. The concentrated solution is then transferred to a flask, and if it has not required filtering, 5 c.c. alcohol are added; but if it has undergone filtration and evaporation, 10 c.c. alcohol must be used; afterwards 30 c.c. are added, the mixture well shaken, 4 c.c. ammonia (sp. gr. 0.960) are next added, the solution shaken until crystals begin to form, and then allowed to stand for 12 hours. The

etheral solution is then poured as quickly as possible on a weighed filter, 20 c.c. ether added, and the flask rinsed round without shaking; the precipitate is thrown on the filter, which is finally washed with 5 c.c. ether. The remaining contents of the flask are then poured on and washed with 5 c.c. water. The flask, with adhering crystals, is dried and weighed. The filter is washed with a further 10 c.c. of water, dried between blotting-paper, and finally at 100° and weighed. This weight, together with the weight of the crystals in the flask, gives the total weight of morphine. A small portion of these crystals, 0.1 gram, is powdered and tested for narcotine by shaking with 30 c.c. lime-water, in which narcotine is insoluble. The results obtained by this method are for the most part accurate, although they are generally too high in the case of adulterated opium.

In assaying tinctures of opium, 120 c.c. of the liquid are taken, evaporated at a low temperature to 10 grams, and treated as above.

L. T. O'S.

**Reaction of Oil of Peppermint.** By A. SCHACK (*Arch. Pharm.* [3], 19, 428—430).—On adding oil of peppermint to fused salicylic acid, a blue-green mass is immediately produced. This, when dissolved in alcohol, is blue by transmitted, but blood-red by reflected light. This reaction has been ascribed to C. Roucher, but the author discovered it in 1878, and he since finds that priority is due to Flückiger, the observations being described in his *Pharm. Chem.* Most acids, and also phenol, dissolved in alcohol, give this reaction, but carbonic anhydride does not, at least under ordinary pressures.

Highly-coloured acetic acid solutions of peppermint-oil absorb all rays of wave-length between 550 and 655 micro-millimeters.

F. L. T.

**Preliminary Notice of a Method for the Quantitative Determination of Urea in the Blood.** By J. HAYCRAFT (*Proc. Roy. Soc. Edin.*, 10, 564—571).—All known processes for determining small amounts of urea in blood are faulty, by reason of the loss of urea during the evaporation of its solutions, more especially if other compounds are in solution. The following process, although still imperfect, reduces the error to 7 per cent.:—100 c.c. defibrinated blood is placed in a dialyser, and 100 c.c. alcohol is poured into the outer vessel. After a time, the blood in the dialyser becomes a cake, and must be removed from the paper and well washed; the alcoholic solution of urea is evaporated down with oxalic acid, and contains but little other organic matter, which may, however, be removed by washing with light petroleum, and the urea then extracted by ethyl acetate. The urea may be estimated by decomposition with sodium hypobromite, with the addition of sugar, which increases the amount of nitrogen given off (Gamgee). Green bile-pigments have been found in the dialysed blood. The condition of the coagulum of blood, whether coarse or fine, depends on the temperature of the coagulating water, and appears to influence the result of the analyses, as the coarser the coagulum, the greater is the difficulty of removing extractives.

E. W. P.

## Technical Chemistry.

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**Colour Photography by Tinting Layers of Coagulated Albumin.** By C. CROS and J. CARPENTIER (*Compt. rend.*, **93**, 1504—1505).—A glass plate is coated with a film of collodion containing 2—3 per cent. of cadmium bromide, and is then dipped in a bath of albumin, prepared by dissolving the whites of twelve eggs in a litre of water. The albumin is coagulated in the collodion by the action of the alcohol and cadmium bromide, and the film thus obtained is saturated with a solution of ammonium dichromate and dried. When exposed to the light, the dichromate acts on the albumin, and renders it incapable of absorbing colouring matters; but where the film is protected from the action of the light, the albumin is unaltered, and can absorb and retain suitable pigments. To obtain coloured images, the plate is subjected to three distinct impressions. In the first the light passes through a screen of some green liquid, the plate being afterwards immersed in a bath of red colouring matter; in the second the screen is orange and the bath blue; in the third the screen is violet and the bath yellow. In this way not only the details, but also the natural colours of the object are faithfully reproduced. For the purposes of illumination, the authors use an electric lamp, before which are placed the screens, consisting of flasks filled respectively with saturated solutions of cobalt chloride, potassium chromate, and copper sulphate.  
C. H. B.

**Treatment of Waste Water.** By E. AUBREY-VITET (*Bied. Centr.*, 1882, 137).—Waste water from a paper factory is mixed with milk of lime, and the deposited mud, when air-dried, contains 15—20 per cent. water. This mud may be used as manure, for it contains 11—15 grams nitrogen and 20—25 grams calcium phosphate per cubic meter of the water.  
E. W. P.

**Notes on Lead Pipes and Lead Contamination.** By W. THOMSON (*Chem. News*, **45**, 116).—The author refers to a case of poisoning through drinking water passing by gravitation through a 1-inch lead pipe. Being asked to suggest a substitute for the lead pipe, he advised the use of a tin-lined lead pipe. However, the water which had passed through this pipe was found to be contaminated with lead to a considerable extent, and on examining some of the tin-lining, this was found to contain a large proportion of lead; in fact, all the samples sent to the author from various manufacturers, on analysis, were found to contain lead, and quickly contaminated water left in contact with them. The author was then informed that in preparing the lining, the tin is poured down the side of a strip of lead into the hole left in the solidified lead in the cylinder, previous to forcing it through the dies by hydraulic pressure. It seemed remarkable that manufacturers who are cognisant of the fact that tin dissolves in lead, should have allowed such a device to be employed for filling the mould. These tin-lined lead pipes are used to a large

extent, and principally in making communication between the beer in the cask and the pump on the counters of beer-retailers. Such pipes would give the idea of safety, but the author has tested many samples of beer passing through such pipes, the result being that the beer contained a considerable proportion of lead. There is another kind of lead pipe manufactured called tinned lead pipe, the inside of which is covered with a very thin coating of a white metal, to afford protection against the action of water on lead. In its preparation the molten tin dissolves the lead, and the coating is a mixture of tin and lead. This coating cannot, therefore, be regarded as a thoroughly efficient protection against the action of water on lead, but tinned lead pipe is much better adapted for use in making communication with the water-mains in large towns than the ordinary lead pipe.

The author has analysed a large number of aerated waters, which he found to be contaminated with lead, from the fact that impure sodium carbonate was used in their manufacture. It was also found that pure water acted more strongly on comparatively pure lead than on lead alloyed with antimony to the extent of  $\frac{3}{4}$  to 1 per cent. D. B.

**Recovery of Nitrogen from Molasses Waste.** By E. KISIELINSKI (*Bied. Centr.*, 1882, 57).—By the patented process employed, 80 per cent. of the nitrogen is recovered as ammonia; the figures published are from 1000 hl. waste there are produced 1650 kilos. ammonium sulphate, 1200 cm. gas, and 600 kilos. tar. By employing the tar as fuel, 600 kilos. coal are saved per day. E. W. P.

**Action of Salt on Molten Copper of Various Degrees of Dryness.** By R. MONGER (*Chem. News*, 45, 80).—In experimenting with salt and copper, it was always noticed that on breaking the button of copper, it had the appearance of tough-pitch metal, whether the metal was dry or not at the commencement of the operation. As the change can only be accounted for by the removal of the cuprous oxide contained in the metal, it was thought that the salt might possibly dissolve it out of the copper. Experiments were made, the results of which prove the correctness of this conclusion, for the following reasons:—(1.) Salt brings dry copper up to tough pitch, being just what poling does, and no doubt exists as to the pole reducing the cuprous oxide. (2.) The amounts lost by the same samples of copper were identical, showing the action to be a definite one. (3.) The amounts lost increase as the dryness of the copper increases, and the only difference between dry and tough pitch coppers is in the amounts of cuprous oxide they contain. (4.) The buttons obtained from the treatment with salt were heated a second time and lost nothing, having already had their cuprous oxide abstracted. The author considers that this is a rapid and easy method for the estimation of cuprous oxide in copper. D. B.

**Preservation of Exposed Bronze Monuments.** By J. W. BRÜHL (*Dingl. polyt. J.*, 243, 251–256).—It is well known that in the course of a few years most statues lose their bronze appearance, becoming covered with an unpleasant black film, and assuming an

appearance like that of iron. This dull dark coloration makes it no longer possible to distinguish the development of the muscles and the finer effects of light and shade. The dark film is said to consist of copper sulphide emanating from the action of sulphuretted hydrogen on the bronze; but this statement is without foundation, as the analyses of the atmosphere of towns show that sulphuretted hydrogen is present in air only in very minute quantities. The green film, the so-called patina, or fine rust, consists of copper carbonate, and if bronzes were destroyed by sulphuretted hydrogen, this rust could not exist, but would be blackened much more readily than pure copper or cupriferous alloys. The author had occasion to investigate the black coating of a bronze statue recently erected at Aachen. Not a trace of copper sulphide could be detected in it. Microscopic examination showed that the film consisted essentially of fine particles of coal, sand, and dust, and analysis gave small quantities of the oxides of copper, tin, zinc, and lead. In order to restore the statue to its original colour, the author, after much investigation, found that by washing with a concentrated solution of ammonium carbonate (1 kilo. per 4 litres water), and subsequently removing the green film with very weak sulphuric acid, the original lustre was brought back. The production of the green film under the black is due to the slow conversion of copper into the carbonate. This film imparts to bronzes the colour desirable from an artistic point of view, and prevents destruction and blackening. Hence ancient bronzes erected in the days long before the introduction of steam boilers and coal fires, have been preserved to our time, the green film originally produced by slow oxidation having protected the bronzes from external actions. The author therefore recommends that bronzes should be preserved by producing this film artificially before erecting them. D. B.

**Preparation of a Solution containing Hypophosphite of Iron, Sodium, Calcium, and Magnesium.** By A. GIBSON (*Pharm. J. Trans.*, **12**, 603—604).—A solution containing ferrous, sodium, and magnesium sulphates in the proportions 1·4 : 2·8 : 1, is added to an equivalent quantity of a boiling solution of calcium hypophosphite containing about 8 per cent. hypophosphorous acid. The filtered solution is mixed with a filtered solution containing 1·8 parts of calcium hypophosphite, 2·6 parts hypophosphorous acid are added, and the whole diluted with 6·6 parts of water.

If the sulphates be mixed with the hypophosphite in the cold solution and allowed to stand, reduction will take place, with formation of sulphuretted hydrogen—



**Sulphur in Zinc-dust.** By A. WAGNER (*Zeits. Anal. Chem.*, **20**, 496).—Attention is drawn to the fact that many samples of zinc-dust contain considerable amounts of sulphur, which may interfere with some of the uses to which the zinc is applied. O. H.

**Direct Deposition of Copper on Cast-iron, Wrought-iron, and Steel.** By F. WEIL (*Compt. rend.*, **93**, 1018—1019, and 1072—

1073).—Copper may be deposited directly on cast-iron, wrought-iron, and steel in a firm homogeneous layer, reproducing all details of ornamentation, &c., by employing an alkaline bath in which cyanides are replaced by organic acids or glycerol. These solutions are not injurious to health; they dissolve oxide of iron without attacking the metal, and thus the surfaces on which the copper is to be deposited are cleaned by the bath itself. Moreover, the organic acids or glycerol are not decomposed, and the strength of the bath is restored by simply adding copper oxide.

Three different methods are employed. In the first the article is placed in the bath in contact with metallic zinc. In the second, which is employed for large articles, the latter are placed in the bath and connected by a thick copper wire with a zinc plate dipping into a solution of soda in a porous cell, the latter being also placed in the bath. When the soda becomes charged with zinc hydroxide, sodium sulphide is added. This precipitates zinc sulphide, and reproduces the sodium hydroxide. In the third method the copper is deposited from the same baths by means of a dynamo-electric machine.

To determine the amount of copper in the depositing liquid, 10 c.c. are mixed with 30—40 c.c. pure hydrochloric acid, heated to boiling, and a standard solution of stannous chloride added until the solution is just decolorised.

Nickel, cobalt, antimony, tin, and other metals, may be deposited directly by the same methods from baths of analogous composition.

The second paper is a claim for priority of invention over Val d'Orne.

C. H. B.

**Maize Cake from Distilleries.** By A. LADUREAU (*Ann. Agronomiques*, 7, 367—370).—When the price of American maize is sufficiently low, certain distillers employ it instead of beet or molasses.

The maize is treated with dilute sulphuric acid or hydrochloric acid under pressure in copper vessels, and the starch is by this means wholly transformed into glucose. The insoluble residue remaining after fermentation is made into maize-cake. The author gives the analysis of five samples:—

Moisture .....	10.50	9.01	7.25	8.52	8.01
Gluten .....	33.12	32.50	41.25	36.25	35.62
Oil .....	11.55	10.27	13.52	12.14	11.50
Starch and dextrin	8.04	9.03	3.27	4.73	5.47
Cellulose .....	24.65	26.85	25.42	27.13	28.20
Extractives .....	9.39	8.54	6.54	6.92	7.47
Calcium phosphate	1.14	2.72	3.75	4.21	3.73
Alkaline salts ....	0.29	0.50			
Other salts .....	1.32	0.58			
	100.00	100.00	100.00	100.00	100.00
Nitrogen .....	5.30	5.20	6.60	5.80	5.70

Maize-cake is thus equal to linseed cake in feeding value, and can be sold much cheaper; as a manure, it is as efficacious as arachida cake, of the same richness in nitrogen.

J. M. H. M.



**Employment of the Maize Residues of Distilleries.** By PORIAN and MÉHAY (*Bied. Centr.*, 1882, 138).—The residues from maize treated with acid may be pressed and washed if to be used as fodder, and then dried. There is no necessity for washing it if it is to be employed as manure.

	Washed for food.	Unwashed for manure.
Nitrogen .....	7.13	6.43
P <sub>2</sub> O <sub>5</sub> .....	1.16	1.19
Oil .....	12.14	12.10
Organic matter .....	69.77	69.61
Ash.....	2.24	2.35
Water.....	7.56	7.32

E. W. P.

**Analysis of Several Malting-barleys.** By K. REISCHAUER (*Bied. Centr.*, 1882, 42).—Malting-barleys differ greatly in composition, the mean percentage of albuminoids being 10. The variation is as follows:—

	N.	Alb.	Ash.	In ash.			
				P <sub>2</sub> O <sub>5</sub> .	SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.
Maximum ....	2.856	17.850	3.340	1.145	0.845	0.0694	0.151
Minimum ....	1.282	8.010	2.120	0.614	0.460	0.0019	0.043
Mean .....	1.729	10.804	2.799	0.902	0.641	0.0200	0.068

E. W. P.

**Condensation of Unfermented Must in a Vacuum.** By J. SUCHY (*Dingl. polyt. J.*, 243, 70—73).—The author had occasion to investigate the condensation of unfermented must, in conjunction with Springmühl, who has patented a process of concentrating grape-juice in a vacuum to one-fifth of the original volume without altering its properties. Trials made with a view of ascertaining whether wine could be condensed and subsequently regenerated, like milk, failed, owing to the presence of alcohol. It was found, however, that the juice of all kinds of grapes can be concentrated without alteration, the degree of condensation depending on the amount of sugar present in the grapes. The husks of the grapes often play an important part in the preparation of wine, and these also were dried in a similar manner. They were subsequently added to concentrated must and made into wine, the quality of which was first class. The author describes the mode of procedure in detail. His object is to remove water from must at the lowest possible temperature without altering its constituents. In the production of wine from condensed must, it is important that the finished wine should have the same colour as the wine prepared directly from the grapes. The husks of grapes impart to wine its colour: hence it is necessary to allow condensed must to ferment with the husks dried according to the above method.

D. B.

**Purification of Beet Juice by Lime.** By H. PELLET and A. NORD (*Bied. Centr.*, 1882, 136).—Experiments show that it is absolutely necessary that more lime should be used than can be dissolved

by the sugar solution, so that complete purification may be obtained. To estimate the quantity of sugar in the waste left after purification with lime, and which generally amounts to 3—4 per cent. of the waste, 20 parts of the well mixed waste is to be dried with 20 parts sand, and 0·2 part ammonium carbonate dissolved in water; it must be so worked that the dried mass is not in a powder, but in lumps as large as peas. This dried mass is then extracted with 15 parts water and 20 parts alcohol for half an hour, the liquid made up to a certain volume, and then examined by the polariscope.

E. W. P.

**Action of Animal Charcoal on Syrup.** By H. PELLET (*Bied. Centr.*, 1882, 135).—A paper by F. Schiller is here referred to, and the author considers that the absorption of sugar by charcoal is analogous to that which occurs during osmose with parchment-paper, for just as much of lime is absorbed by one as by the other.

The carbon of animal charcoal is not the only agent capable of absorbing colouring matters, but all forms of carbon are equally capable of performing this act.

White animal charcoal absorbs lime as well as the black, and if it fails to do this, the failure is due to a glaze formed on the surface by burning.

E. W. P.

**The Strontia Process for the Separation of Sugar from Molasses.** By C. SCHEIBLER (*Bied. Centr.*, 1881, 849—851).—Strontia is better adapted for the separation of sugar from molasses than lime, because the precipitate is granular and not gelatinous. That a good yield should be obtained, at least 3 mols. strontia must be employed, and 4 mols. will precipitate 98·4 per cent. of the sugar. Under increased pressure and temperature, the amount of strontia in the precipitate rises, approaching a tribasic saccharate. The hot precipitate if introduced into hot water is decomposed, strontia crystallises out, and the ordinary saccharate remains in solution. On the large scale, this clear solution is heated over 100°, when the saccharate is precipitated, while the impurities remain in solution; the saccharate is afterwards decomposed by carbonic anhydride.

E. W. P.

**Presence of Phosphorus and Iodine in Cod Liver Oil.** By P. CARLES (*J. Pharm.* [5], 5, 145—147).—The neutral genuine oil from the liver of the cod does not contain phosphorus, and its presence in the brown cod liver oil is due to its being acid, and consequently dissolving out the phosphates in the masses of liver. This is shown by digesting the hepatic parenchyme with neutral oil, and with oil containing free fatty acids from cod liver oil, when in the first case no phosphorus is found in the oil after 24 hours' digestion, whilst in the second the amount of phosphoric acid present increases with the quantity of free acid.

In like manner, iodine is not present in the fresh neutral oil, but only in the brown acid varieties in proportion to their colour and acidity. Its presence is then accounted for on the supposition that the oil on exposure to the air absorbs oxygen, which it converts into ozone, and that, acting on the alkaline iodide contained in the liver, sets the

iodine free, which aided by heat and the fermentation which the brown oils undergo replaces hydrogen in the fatty bodies. L. T. O'S.

**Creaming Milk according to Becker's Method.** By W. FLEISCHMANN and R. SACHTLEBEN (*Bied. Centr.*, 1882, 43—48).—The amount of cream removed increases with the length of time which the milk remains in the apparatus, and the creaming is better when the milk has only been heated to 47—56°; it is also better if the final temperature is 12°, and the milk is less liable to become acid if after heating it be cooled as rapidly as possible.

The curd from skim milk is fine when the milk has been heated for two hours at 60°.

When rennet is employed, the character of the curd remains unaltered up to 64°, only the time for curdling is shortened; at 80°, the curd produced is unfitted for cheese making. Pepsin separates a loose curd from milk heated to 70°. It is not thought possible to keep milk by Becker's process, in which it is heated to 56½°.

E. W. P.

**Becker's Method of Creaming.** By SALSKOWSKI and others (*Bied. Centr.*, 1882, 129).—Milk heated to 75° in closed vessels and then cooled remains sweet for 96 hours; if the vessel is opened, sourness occurs after 48 hours, and if it be heated in the open air, it only remains sweet for 24 hours. A temperature of 50—60° does not alter the taste of milk, and if it be curdled at this temperature, the curd is flocculent. With Laval's separator, E. Greyerz finds that if the cream is cooled with ice only 4—5 per cent. butter is obtainable, but if it be cooled only to 8—10° then 20 per cent. is obtained.

E. W. P.

**Formation of Butter, and its Physical and Chemical Composition.** By V. STORCH (*Bied. Centr.*, 1882, 49—54).—The older theories concerning the condition in which butter exists in milk are considered to be incorrect. Under the microscope the globules of butter appear transparent and smooth, but pressure causes them to solidify and become opaque; at 26·5° butter is formed sooner than at 0°. Between the fat globules, there seems to be a peculiar fluid enclosed in vesicles, and this fluid is of two sorts, the one in minute globules, which causes the fat globules to agglomerate, while the other fluid consists of larger globules of ordinary butter-milk. During the churning, the small globules are caused to agglutinate, and within the lumps so formed is enclosed a peculiar fluid which is different from butter-milk serum, and cements the fat globules to one another. Butter serum is now thought not to be identical with that of milk, but is richer in protein and poorer in sugar, containing 5·8 per cent. of the former and 2·6 per cent. of the latter, as compared with the amount of the same constituents in milk, viz., 3·9 and 4·5. The serum of cream shows a slight increase in protein, and when it is churned, the butter retains more protein than corresponds with the original milk serum: therefore the author thinks that butter contains, besides milk serum, a fluid—which he calls casein hydrate—richer in serum, and varying somewhat in composition according to the length

of time that the cow has been in milk, being higher in cows which have but lately calved; thus the serum of butter from cows that have been long in milk contains one-third, and that of butter from lately calved cows more than half its weight of casein hydrate.

Since casein hydrate is not produced during creaming, it cannot be formed from the nitrogenous matter of the (problematical) cells enclosing the fat globules, as these were present in the cream as well as in the butter. Sour cream contains more casein hydrate than sweet cream, and therefore butter should be formed more quickly if the cream be sour, and this is well known to be the case. The quicker and greater the formation of casein hydrate, so much the more quickly will the butter be produced.

E. W. P.

**A New Class of Colouring Matters.** By H. KÖCHLIN and O. N. WITT (*Dingl. polyt. J.*, **243**, 162—164).—The new colours are prepared by two different methods: (1.) By the action of nitroso-derivatives of tertiary aromatic amines or phenols, or of imido-chloroquinones or their homologues on alkaline solutions of phenols at the ordinary or at an elevated temperature. The formation is facilitated by the addition of reducing agents. (2.) A mixture of a paramido-derivative of an aromatic amine or phenol is oxidised, together with phenol, in weak alkaline or weak acid (acetic acid), or better, in perfectly neutral solution. The authors call these colours "indophenols," as indicating their origin, and simultaneously to show their analogy to indigo. The  $\alpha$ -naphthol derivative is essentially important. It is obtained by reducing nitrosodimethylaniline in a weak hydrochloric acid solution with zinc-dust, and adding an alkaline solution of  $\alpha$ -naphthol and potassium dichromate; after mixing, acetic acid is added gradually. The colouring matter is formed immediately, and is entirely precipitated as soon as the alkaline solution becomes acid. It is filtered, washed, and pressed into cakes. The derivative of  $\alpha$ -naphthol is blue; phenol gives a greenish tinge; resorcinol and  $\beta$ -naphthol form a violet. The air-dried precipitate consists of a blue mass of conchoidal fracture resembling Guatemala indigo; it dissolves in concentrated sulphuric acid with a deep blue colour. It is sparingly soluble in alcohol, more easily soluble in phenol, and when heated it slowly sublimes in the form of fine blue needles resembling indigo. Its application in dyeing shows further analogies to indigo. For wool dyeing, the precipitate is reduced with grape-sugar in an alkaline solution at 80°, the surface of the solution assuming a green colour with copper-coloured stripes resembling an indigo vat: after dilution with a large quantity of hot water, the wool is steeped in this bath until the desired shade has been produced. It is then washed with water, and oxidised by exposure to the air, or, better, by passing through an oxidation-bath. The dyed wool stands all cleaning operations, but is acted on by strong mineral acids. The authors have patented several economical processes of producing blues directly on the fibre. (1.) The cloth is blocked with a solution of naphthol in soda, then printed with a thickened mixture of nitrosodimethylaniline hydrochloride and a reducing agent, active only in the presence of alkalis, *e.g.*, stannous oxide, grape- or milk-sugar. The colour is developed after steaming. (2.) The cloth is blocked with

the reducing agent and printed with a thickened mixture of nitroso-dimethylaniline and sodium naphtholate. The colour appears on steaming. (3.) The cloth is printed with a thickened solution of amidodimethylaniline and sodium naphtholate, steamed and passed through a bath of potassium dichromate.

In conclusion, it is mentioned that although these colours are affected by acids more easily than indigo prepared from the propiolic acid, they nevertheless resist soap and chlorine better. They are considerably cheaper and stand the light better than indigo. Propiolic acid does not stand steaming, whilst indophenol is developed by means of steaming; it may therefore be used in combination with all other steam colours.

D. B.

**Fixation of Alumina as a Discharge on Indigo-blue by means of Aluminium Chloride.** By G. SAGET (*Chem. News*, 45, 113).—The property of hydrated aluminium chloride to be decomposed into alumina and hydrochloric acid when dried, may be used for obtaining a discharge on indigo-blue, whilst alumina is deposited where the chloride has been printed, and may serve as a mordant for various colours. On adding manganese peroxide to the aluminium chloride, Scheele's reaction is obtained upon the tissues, the nascent chlorine destroying the colouring matter and producing whites. The following discharge is printed upon a medium indigo-blue:—80 grams manganese peroxide, 300 grams aluminium chloride, 200 grams calcined starch, 420 grams water. After printing, the pieces are steamed without pressure for an hour and a half, letting the vapours escape. Thus a design of a pinkish-white is obtained which is cleared by a passage through weak hot hydrochloric acid. If the alumina is intended to serve as the mordant for a colour, the pieces are washed in hot water, then in cold water and dyed. Thus the author has obtained on indigo-blues fine designs in alizarin reds, fustic, or quercitron-yellow, coerulein-green, &c. For a light or dark indigo-blue, this discharge must be let down or strengthened in proportion. A precaution to be taken when preparing this discharge is to add the aluminium chloride last, otherwise clots are formed very difficult to get rid of. Lead peroxide gives an analogous reaction with aluminium chloride.

D. B.

**Valuation of Meat.** By C. VIRCHOW (*Bied. Centr.*, 1881, 775—780).—Analyses were made of the amount of water and extract in the flesh of different animals, in the hopes that they would allow of the introduction of a method whereby the value of meat might be determined; but the differences observed are so slight that no results of any value have been obtained. Veal contains more water than beef, whilst lean beef has less than well-fed beef, and the water in un-healthy meat is greater than in sound meat. The same holds good for the extract.

E. W. P.

## General and Physical Chemistry.

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**Band-spectrum of Air.** By E. GOLDSTEIN (*Ann. Phys. Chem.* [2], 15, 280—289).—It is pointed out that the generally accepted assumption is no longer tenable, that the electric spectrum of a gas, at least in so-called positive light, remains constant, and does not change its "order," and that, therefore, its general form can be determined by a single observation in any form of tube, and within wide limits of rarefaction. The air-spectrum does in fact vary considerably within relatively narrow limits of density. This easily accounts, not only for the great differences between the results of different observers, but also for those obtained by the same observer, and more especially those of Plücker and Hittorf (*Phil. Trans.*, 1865, 1), whose conclusions as to the existence of nitrogen in two allotropic modifications are erroneous.

By increasing the rarefaction, the ordinary spectrum of positive light gradually changes into the cathode-spectrum. The wider the tube the greater is the rarefaction required. The discharge is interrupted before the change takes place if the tubes are more than 1—1·5 cm. wide. Very narrow tubes (0·2 mm. and less), however, offer too great a resistance for the passage of the spark. The conversion of the positive into the negative spectrum can be observed even with the naked eye. The positive light loses its reddish-yellow or chamois-red colour, and becomes successively flesh-coloured, lilac, and finally blue.

A particular form of the spectrum is not determined solely by the degree of rarefaction, but an approximation to the cathode-spectrum may likewise be produced, within certain limits, by increasing the strength of the discharge.

T. C.

**Spectroscopic Observations with Monochromatic Light.** By C. V. ZENGER (*Compt. rend.*, 94, 155—156).—The paper points out the advantages of a dispersion apparatus formed by the combination in a parallelepipedon of two prisms, having very different indices for red and violet light, and equal indices for light of mean refrangibility. By selecting suitable liquids, and making use of total reflection, observations may be made in the spectroscope with light of any required refrangibility. The author has found that benzene and benzyline combined with quartz eliminate the extreme red rays under an angle of about 75°, whilst pure anethol eliminates the extreme violet rays for the same refractive angle. This apparatus allows the protuberances and the reversed colours of the sun's chromosphere to be advantageously observed with a wide slit, and the extraordinary sharpness of the spectroscopic image permits the use of higher magnifying powers than have hitherto been applied. Photographs obtained by this means have greater sharpness than with any other kind of spectroscope.

R. R.

**Violet Phosphorescence of Calcium Sulphide.** By W. DE W. ABNEY (*Phil. Mag.* [5], 13, 212—214).—The calcium sulphide used

was such as is employed in Balmain's luminous paint. The emission-spectrum was examined, and it was found that the greatest luminosity is between G and F, and a feebler one extending from between E and F, as far as the eye can recognise colour of low intensity, towards the red. There was no trace of any radiation in the ultra-violet. It could not be positively determined whether there is any radiation below the red, but the gradually increasing brightness of the spectrum in the yellow seems to show that there is. The part of the spectrum of the electric light which excited phosphorescence extends somewhat beyond H on the one hand, and G on the other. The ultra-violet rays do not seem to cause phosphorescence in this case. The rays which destroy the phosphorescence were also determined, and are shown in a map accompanying the original paper. In the infra-red region there is a portion which does not destroy it, and curiously enough the wavelengths of this portion are octaves to the exciting portion of the spectrum about G and H. There were also indications of another octave below the second band. It is immaterial whether the phosphorescence be excited by the indigo or violet rays. T. C.

**Electro-optic Experiments on Various Liquids.** By J. KERR (*Phil. Mag.* [5], 13, 153—169).—This is a continuation of previous work on the subject (*ibid.*, August and September, 1879). The elements bromine, phosphorus, and sulphur are all strongly positive in the liquid state. The hydrocarbons are, without exception, non-conductors and purely positive. Amongst the hydrocarbons, great density is generally accompanied by high electro-optic power. The common alcohols are negative as a class. From the higher members downwards, the negative electro-optic power diminishes regularly, until it passes in the last stage of the series (ethyl to methyl) from feebly negative to feebly positive. Distilled water is also distinctly positive. Fatty acids, which are liquid at the ordinary temperature, are in constant opposition of sign to the corresponding alcohols; they are also very much stronger. Only two solid fatty acids have been examined in the state of fusion, and are then strongly negative. Of other alcohols and acids, allyl, benzyl, and cinnyl alcohols are negative; glycol and glycerol are feebly and impurely negative; phenol is positive, although its chemical relations are rather those of an alcohol than of an acid; oleic and lactic acids are both positive, the former strong, the latter very feeble. Ethyl and amyl oxides are purely negative, and stronger than the corresponding alcohols. Amyl oxide is a moderately good insulator, and one of the best negative dielectrics yet known. The haloïd ethers are purely positive, and rise in power from one series to another in the order, I, Br, Cl; they generally rise also in power from lower members upwards. Some of them show an extraordinary increase of insulating and electro-optic powers as the experiment proceeds. Amyl chloride is one of the best positive dielectrics known; amyl bromide also is very strong. T. C.

**Thermic Laws of the Discharge Spark of a Condenser.** By E. VILLARI (*Compt. rend.*, 92, 1449—1452).—The discharge spark of a condenser is one which is produced directly against the discharger.

By means of a discharge thermometer, described in the original paper, the properties of this spark have been studied with the following result:—The heat developed by the spark is proportional to the quantity of electricity multiplied by the electric density, or, for the fall in potential, is proportional to the quantity of electricity. T. C.

**Galvanic Elements which consist only of Elementary Substances, and the Electric Conductivity of Bromine and Iodine.** By F. EXNER (*Ann. Phys. Chem.* [2], 15, 412—439).—It has been generally supposed that in any galvanic element one at least of the constituents must be an electrolyte. The author shows that this condition is unnecessary, having constructed galvanic elements of elementary bodies only, viz., of carbon, and a metal immersed in bromine or iodine respectively. He has determined the electromotive force of the following combinations with the results given below:—

Element.	Electromotive force.		Element.	Electromotive force.	
	Observed.	Calculated.		Observed.	Calculated.
Mg   Br   C ..	2·36 D	—	Mg   I   C ...	1·57 D	—
Al   Br   C....	1·60 „	1·61 D	Zn   I   C ....	0·96 „	0·98 D
Zn   Br   C ...	1·52 „	1·52 „	Al   I   C ....	0·77 „	0·93 „
Pb   Br   C ...	1·29 „	1·29 „	Hg   I   C....	0·55 „	0·68 „
Ag   Br   C ...	0·91 „	0·91 „	Ag   I   C....	0·56 „	0·55 „
Cu   Br   C ...	0·51 „	0·65 „	Pt   I   C ....	0·013 „	—
Pt   Br   C....	0·04 „	—	—	—	—

In the bromine or iodine, the current goes from the metal to the carbon. Iodine conducts the current in both the solid and liquid condition, and there is no apparent polarisation with either bromine or iodine. As a general rule, however, iodine does not give such good results as bromine, for in the case of the metals Cu, Pb, and Fe, a constant element is not obtained, but the values obtained gradually diminish from the moment of immersion, until the electromotive force becomes *nil*. This is evidently due to the fact that these metals are covered almost instantaneously with a solid film of the resulting compound.

The above results show that elementary bodies which act chemically on one another are capable of forming galvanic elements; whilst if the contact theory be maintained, it will be necessary to assume that certain combinations of elements obey Volta's law of tensions, whilst others do not. There is, in fact, no case known in which chemical action is unaccompanied by a development of electricity, or an evolution of electricity unaccompanied by chemical action.

The electric conductivity of bromine and iodine at different temperatures was found to be as follows:—



Bromine.		Iodine.	
<i>t</i> .	Conductivity.	<i>t</i> .	Conductivity.
— 5.5	794.10 <sup>-16</sup>	17 (solid)	572.10 <sup>-14</sup>
0	863.10 <sup>-16</sup>	110 (liquid)	120.10 <sup>-10</sup>
17.2	1208.10 <sup>-16</sup>	115 „	129.10 <sup>-10</sup>
38.5	2503.10 <sup>-16</sup>	120 „	137.10 <sup>-10</sup>
		143 „	172.10 <sup>-10</sup>
		166 „	211.10 <sup>-10</sup>

These numbers show that bromine and iodine conduct without polarisation, *i.e.*, like metals, whilst, unlike metals, their conducting power increases with the temperature, and that considerably. Bromine is by far the worst of all known conductors, the resistance offered by a column of bromine 1 meter long being more than equal to that of a column of mercury of the same cross section, and as long as the diameter of the planetary system. T. C.

**Experiments with the Faure Secondary Battery.** By ALLARD, F. LE BLANC, JOUBERT, POTIER, and TRESKA (*Compt. rend.*, **94**, 600—604).—The experiments were made with a battery of 35 elements of the new form, charged by means of a Siemens machine, and discharged through a series of Maxim lamps. 90 per cent. of the total quantity of electricity stored up in the pile was given out during the discharge. The exterior electrical work done during the discharge was equal to 0.40 of the total work done in charging the pile, or 0.60 of the total quantity of work actually stored up, the pile being charged under a mean potential of 91 volts, and discharged under a mean potential of 61.5 volts. If *E* represents the electromotive force of the pile, *R* its internal resistance, *I* the intensity of the current, and *t* its duration whilst charging the pile, and *E'*, *R'*, *I'*, and *t'* respectively the corresponding quantities during the discharge, the yield of electricity is given by the expression—

$$\alpha = \frac{I'(E' - R'I')t'}{I(E - RI)t},$$

or removing *I't'*, *It*, and assuming that *E* = *E'*,

$$\alpha = \frac{E - R'I'}{E + RI}.$$

It is evident that the yield will always be less than unity, but will be greater the smaller the intensities and resistances. It is therefore more economical to charge with the weakest possible current, and prolong the time of charging. C. H. B.

**Variation of the Electric Conductivity of Glass with Temperature, Density, and Chemical Composition.** By T. GRAY (*Chem. News*, **45**, 27).—On examining a large number of lime glasses, it was found that as their composition approached more nearly to that of a mixture of trisilicates, so did their conductivity decrease. The same was found to hold with lead glass, in which the density varies with the composition. H. B.

**Electrical Resistance of Gases.** By E. EDLUND (*Phil. Mag.* [5], 13, 200—212).—The resistance offered by gases to the propagation of electricity differs from that offered by solids and liquids in the following respects :—

*Solids and Liquids.*—There is no need of a certain amount of electromotive force for the passage of a current. The quantity of heat produced during its passage is proportional to the square of the intensity of the current, and is inversely as the cross section of the conductor. The resistance is inversely proportional to the section of the conductor. The difference between the electroscopic tensions on two points situated at a certain distance the one from the other is proportional to the product of the resistance between those two points multiplied by the intensity of the current.

*Gases.*—In order that a current may traverse a gas there must be a certain amount of electromotive force, which depends on the nature, density, and temperature of the gas, but never falls below a certain limit in given circumstances, for if so the gas becomes a perfect insulator. The quantity of heat produced by the passage of the current is proportional to the intensity of the current, and not to its square, and is independent of the cross section of the gas. The resistance of the gas is also independent of the section of the containing tube. The difference between the electroscopic tensions at two points situated at a distance from one another in a column of gas is quite independent of the intensity of the current. Gases begin to be conductors when heated to the temperature of redness, after which their conductivity increases in proportion as the temperature rises above that point, and also as the density of the gas diminishes. The resistance of a gas is nearly inversely proportional to the intensity of the current.

The above differences between gases on the one hand and solids and liquid conductors on the other may be fully explained by the unitarian theory of the nature of electricity proposed by the author, if we admit that the resistance of a gas is independent of the intensity of the current.

According to this theory, the galvanic current in a closed circuit consists in the free ether present in the circuit being set in translatory motion. The intensity of the current is determined by the quantity of ether passing in the unit of time through any section of the conductor; and the velocity of the ether for equal intensity of current is inversely proportional to the magnitude of the section.

The conclusion arrived at is that, so far as solids and liquids are concerned, the galvanic resistance is proportional to the intensity of the current. This is opposed to the opinion generally held, but must be true unless we assume that the fluid termed electricity is governed by laws of motion quite different from those to which other fluids are subject. Nor is the above conclusion contrary to experimental results.

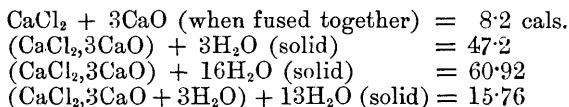
If we assume that electromotive force is measured by the acceleration which it can impart in the unit of time to the unit of mass, then Ohm's law can easily be deduced from ordinary mechanical principles. The electromotive force is shown to be independent of the intensity of the current. The theory likewise explains the production and distri-

bution of free ether at the surface of a galvanic conductor. The circulating ether supposed to be concerned, according to the above theory, in electrical phenomena, possesses the properties of ordinary gases, in that the mobility of its molecule is considerable, so as to permit it to exert equal pressures in all directions, the only difference being that the ether, whether compressed or expanded, will place itself at the surface of the galvanic conductor, since the ether molecules repel each other.

It is shown that the *difference between the electroscopic tensions of two planes is proportional to the intensity of the current, multiplied by the principal resistance between those planes.* T. C.

**Heat of Formation of Water.** By A. SCHULLER (*Ann. Phys. Chem.* [2], 15, 292—297).—A reply to criticisms by v. Than on this subject. T. C.

**Heat of Formation of Calcium Oxychloride.** By G. ANDRÉ (*Compt. rend.*, 92, 1452—1454).—The crystallised oxychloride,  $\text{CaCl}_2 \cdot 3\text{CaO} + 16\text{H}_2\text{O}$ , obtained by boiling the oxide with a solution of calcium chloride, develops heat = + 63·4 cal. when dissolved in dilute hydrochloric acid. It loses water when dried in a vacuum, until its composition corresponds with  $\text{CaCl}_2 \cdot 3\text{CaO} + 3\text{H}_2\text{O}$ . This latter compound, when dissolved in dilute hydrochloric acid, develops 97·8 cal. A product, obtained by fusing together 1 mol.  $\text{CaCl}_2$  with 3 mols.  $\text{CaO}$ , develops 147·2 cal. when similarly treated.



This last quantity is greater than the heat of hydration of calcium chloride, and hence explains the formation of the oxychloride in presence of water. T. C.

**Decomposition of the Haloïd Salts of Mercury by Haloïd Acids and by the Haloïd Salts of Potassium.** By BERTHELOT (*Compt. rend.*, 94, 604—612, and 677—683).—The heat of formation of mercuric chloride,  $\text{HgCl}_2$ , is + 22·0 cal.; of mercuric bromide, 30·8 cal.; of the iodide, red, 46·4 cal.; yellow, 43·4 cal. A similar relation exists between the heats of formation of the haloïd silver salts, although the heat of combination of potassium with each halogen is practically the same. The heat of formation of mercuric cyanide,  $\text{HgCy}_2$  = + 33·6 cal.

Mercuric iodide (red) dissolves readily in dilute hydriodic acid (1 equivt. in 2 litres), with development of heat = + 4·8 cal., a quantity practically identical with the heat of solution of mercuric iodide in a dilute solution of potassium iodide. The amount of heat developed is the same with a solution of hydriodic acid of half the strength (1 equivt. in 4 litres). Mercuric bromide dissolves in hydrobromic acid with development of heat, but the amount developed varies with the relative proportion of acid and the degree of dilution.

The heat of solution of mercuric chloride in hydrochloric acid (1 equivt. in 2 litres) is only + 1.0 cal., a quantity practically equal to the heat of solution of mercuric chloride in a solution of potassium chloride (0.8 cal.). The heat of formation of hydromercuric chloride is less than that of hydromercuric bromide, and that of the bromide less than that of hydromercuric iodide. This indicates that the dissociation of the acid salts in solution increases as the atomic weight of the halogen decreases, a fact which agrees with the chemical properties of the solutions.

Hydrocyanic acid completely displaces hydrochloric acid from mercuric chloride in solution, with development for  $\text{HgCy}_2$  of + 10.8 cals. The addition of potassium cyanide to excess of mercuric chloride in dilute solution, is accompanied by a development of heat which is independent of the proportion of mercuric chloride, and for  $\text{KCy}$  (65.1 grams) = 17.0 cals., a number corresponding with complete double decomposition and formation of mercuric cyanide and potassium chloride. On the other hand, when potassium cyanide is in excess, the heat developed for each mol.  $\text{HgCl}_2$  (271 grams) = + 46.8 cals., a number corresponding with the conversion of the mercuric cyanide into the double cyanide  $\text{HgCy}_2 \cdot 2\text{KCy}$ . Lastly, the addition of 1 mol.  $\text{HgCl}_2$  to 1 mol.  $\text{HgCy}_2 \cdot 2\text{KCy}$  in dilute solution, develops + 20 cals., corresponding with the conversion of the double salt into mercuric cyanide and formation of potassium chloride.

When mercuric bromide and hydrocyanic acid, or mercuric cyanide and hydrobromic acid are mixed together, an interchange of elements takes place to an extent dependent on the relative proportions of the different compounds and the dilution of the solutions. The maximum development of heat, which accompanies the change, corresponds with the almost complete conversion of the mercury into mercuric cyanide.

When potassium cyanide is added to mercuric bromide, the heat developed corresponds with the almost complete conversion of the mercuric bromide into cyanide. The change is, however, not complete, for the addition of potassium bromide to mercuric cyanide develops a small quantity of heat, owing to the formation of a double salt,  $\text{HgCy}_2 \cdot \text{KBr}$ , increasing in amount with an increase in the proportion of mercuric cyanide. If the potassium cyanide is in excess, the double cyanide  $\text{HgCy}_2 \cdot 2\text{KCy}$  is formed, with development of heat for 1 mol. = 34.6 cals. This double cyanide is decomposed by mercuric bromide, with formation of potassium bromide and mercuric cyanide, and development of + 12.8 cals.

Mercuric cyanide is completely decomposed by hydriodic acid, with formation of mercuric iodide, and development, for each molecule  $\text{HgCy}_2$ , of + 16.0 cals. This result is due to the fact that the heat of formation of mercuric iodide is greater than that of the cyanide, whereas the heat of formation of the latter is greater than that of either the bromide or chloride. If the hydriodic acid is in excess, a soluble acid salt is formed, with an additional development of heat = + 5.6 cals. On the other hand, when mercuric iodide is agitated with a solution of hydrocyanic acid, a small quantity dissolves, with slight reduction of temperature, owing to the formation of acid salts.

When mercuric iodide is mixed with potassium cyanide in excess, the maximum development of heat (19.8 cal. for 1 mol.  $\text{HgI}_2$ ) corresponds with the formation of the double cyanide  $\text{HgCy}_2 \cdot 2\text{KC}_y$ . When mercuric cyanide is added to potassium iodide, the compound formed depends on the relative proportions of the two salts. If the cyanide is in excess, the double salt  $\text{HgI}_2 + \text{HgCy}_2 \cdot 2\text{KC}_y$  is formed, with development of heat for each molecule  $\text{KI} = 3.0$  cal. If, on the other hand, the iodide is in excess, the maximum development of heat corresponds with the simultaneous formation of the double iodide  $\text{HgI}_2 \cdot \text{KI}$ , and the double cyanide  $\text{HgCy}_2 \cdot 2\text{KC}_y$ . The extent of the change varies with the degree of dilution and the relative proportions of the reacting bodies.

In the first paper, a table is given of the heats of formation and solution of the principal double haloid compounds of mercury.

C. H. B.

**Double Salts of Mercury.** By BERTHELOT (*Compt. rend.*, **94**, 482—488, and 549—554).—The formation of potassio-mercuric iodide from dry potassium iodide and red mercuric iodide develops + 2.1 cal.; from the yellow iodide, + 5.1 cal. The heat of formation of the hydrate  $\text{KI} \cdot \text{HgI}_2 + \text{H}_2\text{O}$ , from liquid water and the red iodide = + 2.3 cal.; from the yellow iodide, + 5.3 cal. Potassio-mercuric iodide exists in solution. The salt should be dried at as low a temperature as possible, since it undergoes partial dissociation on fusion.

Mercury chloriodide is not formed in dilute solutions, or its formation develops no sensible amount of heat. When equivalent quantities of mercuric chloride and iodide are fused together, a yellowish liquid is obtained which solidifies on cooling to a clear yellow crystalline mass. This may be powdered without undergoing alteration, but after some time red mercuric iodide separates out, and the change takes place much more rapidly in the powdered substance. Recently fused mercuric chloride and bromide develop more heat on solution than when they have been prepared for some time, probably owing to a partial retention of their heat of fusion, as previously observed in the case of chloral hydrate and alcoholate. The heat developed by the solution, in potassium cyanide solution, of powdered mercuric chloriodide which has been prepared for some time, is sensibly equal to the sum of the respective heats of solution of the chloride and iodide. If, however, the recently fused and cool double salt is dissolved in potassium cyanide solution without being powdered, the heat developed is 3.2 cal. more; if the salt is previously powdered, it is 2.2 cal. more. This difference is greater than the sum of the difference observed in the case of mercuric chloride (+ 0.4 cal.) and the heat developed by the conversion of yellow mercuric iodide into the red variety (+ 1.5 cal.).

No heat is developed on mixing fused mercuric chloride with the fused iodide, chloride with bromide, or iodide with bromide.

The formation of mercuric chlorobromide in both the wet and dry way develops no sensible amount of heat. The formation of orange mercuric bromiodide in the wet way also develops no sensible amount of heat. When equivalent quantities of the bromide and iodide are

fused together, they yield a yellowish salt, which is very stable and only dissociates with extreme slowness. Its heat of solution in potassium cyanide solution is sensibly equal to the sum of the respective heats of solution of its constituents. The heat of formation of mercuric chlorocyanide,  $\text{HgClCy}$ , a well crystallised salt, is practically *nil*; the formation of the bromocyanide and iodocyanide, however, appears to be accompanied by a development of heat.

*Potassio-mercuric iodocyanide*,  $(4\text{KI}, \text{HgCy}_2 + \text{H}_2\text{O})$ , forms long needles. The heat of formation of the anhydrous salt,  $\text{KI}, \text{HgCy}_2 = +6.5$  cal.; that of the hydrated salt,  $4(\text{KI}, \text{HgCy}_2) + \text{H}_2\text{O} = +27.6$ ; the difference being practically equal to the heat of fusion of the water. When the iodocyanide is carefully heated, it first yields a sublimate of yellow mercuric iodide, and is afterwards decomposed with liberation of mercury and cyanogen. It must be regarded as formed by the union of mercuric iodide with potassio-mercuric cyanide. This view is supported by the thermal phenomena accompanying its formation. *Potassio-mercuric bromocyanide* forms beautiful crystals. The formation of the anhydrous salt,  $\text{KBr}, \text{HgCy}_2$  develops  $+3.9$  cal.; that of the hydrated salt,  $2(\text{KBr}, \text{HgCy}_2) + 3\text{H}_2\text{O}$ , develops  $+9.4$  cal. When the anhydrous salt is gently heated it gives no sublimate of mercuric bromide; when more strongly heated it blackens and decomposes with evolution of mercury and cyanogen and formation of a sublimate of mercurous bromide. It cannot be regarded as a triple salt. *Potassio-mercuric chlorocyanide* is a crystalline salt. The formation of the anhydrous salt,  $\text{KCl}, \text{HgCy}_2$ , develops  $+1.6$  cal.; that of the hydrated salt,  $\text{KCl}, \text{HgCy}_2 + \text{H}_2\text{O}$  develops  $+3.0$  cal. When gently heated the salt yields no sublimate. At a higher temperature it blackens and decomposes, mercury and cyanogen being given off, whilst small quantities of mercuric and mercurous chlorides also sublime.

C. H. B.

**Velocity of the Propagation of Explosion in Gases.** By BERTHELOT and VIELLE (*Compt. rend.*, **94**, 101—108).—The authors have studied the velocity of the propagation of the explosion of detonating mixtures of gases in very long tubes. Their results show that this velocity is independent of the length and material of the tube, is the same whether the tube be open or closed, straight or curved, and remains unaffected by changes of pressure within the limits of the experiments (*i.e.*,  $\frac{3}{4}$  to 2 atmospheres). In very narrow tubes (1.5 mm. diameter) the velocity is diminished, and the introduction of inert gases has the same effect. The velocity varies with the nature of the detonating gas, being for the mixture  $\text{H}_2 + \text{O}$  2810 metres per second, whilst for  $\text{CO} + \text{O}$  it is only 1089 metres per second.

R. R.

**The Explosive Wave.** By BERTHELOT (*Compt. rend.*, **94**, 149—152).—In this paper, the author observes that the explosion propagated in a mixture of gases is a very different action from a sonorous vibration. The theoretical relation between the velocity of the wave of explosion and the chemical nature of the gas is difficult to determine, as it depends on the temperature, which is not the same in the

combustion of two different systems. The inequalities observed relate not only to the quantities of heat developed, but to the uncertainty of the values of the specific heats at high temperatures, and are affected by dissociation. Nevertheless, since the total energy of the gas at the moment of explosion depends on its initial temperature and the heat disengaged during the combustion, these data determine the absolute temperature of the system, which is also proportional to the *vis viva* ( $\frac{1}{2}mv^2$ ) of the gaseous molecules. The velocity of translation is therefore proportional to the square root of the ratio between the absolute temperature,  $T$ , and the density of the gas referred to air, or according to Clausius,—

$$v = 29\cdot354^m \sqrt{\frac{T}{\rho}}.$$

If we assume for  $T$  the value of 3000, which is admitted by most chemists and physicists, the velocity of translation of the gaseous molecules at the temperature developed by the combustion, would be about 1300 m. per second for carbonic acid, and 2000 to 2500 m. for oxyhydrogen gas, according as the vapour of water is supposed to be more or less dissociated. These figures are precisely of the order of magnitude observed in the experiments. Analogous agreements are obtained when the calculation is made for various admixtures of air.

R. R.

**Compressibility of Gases.** By E. SARRAU (*Compt. rend.*, **94**, 639—642, and 718—720).—From the results of Amagat's experiments (see Abstr., 1881, 12, 782, 1094) the author has calculated the constants in Clausius' expression for the relation between the pressure, volume, and absolute temperature of a gas—

$$p = \frac{RT}{v-\alpha} - \frac{k}{T(v-\beta)^2},$$

for oxygen, carbonic anhydride, nitrogen, and methane, the unit of pressure being the pressure of the atmosphere, and the unit volume the volume of the gas at 0° C. and atmospheric pressure.

*Oxygen*:  $R = 0\cdot003663$ ,  $k = 0\cdot5475$ ,  $\alpha = 0\cdot000890$ ,  $\beta = 0\cdot000686$ .

The values of the variables at the critical point are:—

$$v_c = 0\cdot004042, t_c = -105\cdot4, p_c = 48\cdot7 \text{ atmos.}$$

The density of liquid oxygen, calculated from these numbers, is 1·055, a result which confirms Pictet's determination.

*Carbonic anhydride*:  $R = 0\cdot003663$ ,  $k = 2\cdot0920$ ,  $\alpha = 0\cdot000866$ ,  $\beta = 0\cdot000949$ .

The values of the variables at the critical point are:—

$$v_c = 0\cdot004496, t_c = +32\cdot0^\circ, p_c = 77\cdot0 \text{ atmos.}$$

The formula no longer represents the experimental results when the volume of the gas is less than that given in the table.

*Nitrogen*:  $R = 0\cdot003663$ ,  $k = 0\cdot4464$ ,  $\alpha = 0\cdot001359$ ,  $\beta = 0\cdot000263$ .

The values of the variables at the critical point are:—

$$v_c = 0\cdot004603, t_c = -123\cdot8^\circ, p_c = 42\cdot1 \text{ atmos.}$$

*Methane*:  $R = 0.003663$ ,  $k = 0.9295$ ,  $\alpha = 0.001091$ ,  $\beta = 0.000840$ .

The values of the variables at the critical point are:—

$$v_c = 0.004953, t_c = -75.7^\circ, p_c = 46.8 \text{ atmos.}$$

The numbers calculated by means of these constants agree closely with those actually obtained. C. H. B.

**Expansion of Water by the Absorption of Gases.** By K. ANGSTRÖM (*Ann. Phys. Chem.* [2], 15, 297—308).—The observations were made with air, nitrogen, carbonic oxide, oxygen, hydrogen, and carbonic anhydride.

The law previously observed by Mackenzie and Nichols (*Wied. Ann.*, 3, 134), and by Nichols and Wheeler (*Phil. Mag.* [5], 11, 113), as regards carbonic anhydride and ammonia, is confirmed, viz., *that the increase in volume of the water is proportional to the amount of gas absorbed.*

The increase in volume of water, when saturated by the several gases, is as follows:—

Nitrogen.....	0.0000294	
Air .....	0.0000346	
Carbonic oxide .....	0.0000418	
Oxygen .....	0.0000474	
Hydrogen .....	0.0000204	
Carbonic anhydride .....	$\left\{ \begin{array}{l} 0.002246 \\ 0.002389 \end{array} \right.$	T. C.

**Tension-differences between a Metal and Liquids of Different Concentration.** By E. KITTLER (*Ann. Phys. Chem.* [2], 15, 390—412).—In a former communication (*Wied. Ann.*, 12, 572), Volta's law of tensions was shown to hold good for a series of various liquids. The investigation has been further extended to other liquids with the following results:—

1. The electromotive force was determined for the combination  $\text{Cu}|\text{L} + \text{L}|\text{CuSO}_4 + \text{CuSO}_4|\text{Cu}$ , in which L represents a concentrated solution of a chloride of one of the following metals: potassium, sodium, ammonium, lithium, calcium, strontium, barium, magnesium, manganese, nickel. The order of electromotive power remains the same if distilled water be substituted for a solution of copper sulphate. 2. The electromotive power diminishes with the degree of concentration of the chloride solution. 3. The current goes from the chloride to the sulphate, and from the more concentrated to the dilute solution. 4. Volta's law of tensions holds good for various percentage solutions of the above chlorides in contact with distilled water or sulphate of copper solution. 5. A different series of electromotive powers is obtained if sulphuric acid is used in place of copper sulphate solution, but in this case also the electromotive power diminishes with the degree of concentration, and is even more marked. The current passes from the chloride to the acid, but with very dilute solutions from the acid to the chloride. 6. Volta's law does not hold in the case of chlorides in contact with sulphuric acid. T. C.



**The Liquid and Gaseous States.** By J. B. HANNAY (*Compt. rend.*, 92, 1336—1337).—This is merely a note to claim priority of communication. Cailletet and Hautefeuille, in a memoir entitled "Researches on Change of State of Temperatures bordering on the Critical Point," communicated to the Academy on April 4, 1881, explain, that after having given a blue colour to carbonic anhydride by dissolving oil of galbanum in it, they are enabled to show that the striæ observed by Andrews are really produced by layers of liquid and gas superposed upon each other, and that they have come to the conclusion that matter does not pass insensibly and by degrees from the liquid to the gaseous state. In a note communicated to the Royal Society, dated May 24, 1880, "On the Condition of Fluids at their Critical Temperatures," the author made a precisely similar statement; but whereas the method of Cailletet and Hautefeuille is applicable only to the critical pressure, which is necessarily low, for at high pressures the oil is equally soluble in liquid and in gaseous carbonic anhydride, the method, explained in detail in the above-mentioned memoir, and in another entitled "Meniscus and Capillarity Observations of a Liquid at different Temperatures and under Varying Pressures," renders it possible to examine the condition of the fluid at pressures which may exceed five times at least the critical pressure. It was thus established that at this pressure (nearly 300 atmospheres) the meniscus of a liquid disappears at the same temperature as when it is submitted to the pressure of its own vapour, which shows that the liquid state ends at the critical temperature, whatever be the pressure. The author states that consequently more than a year ago he proved for all pressures what Cailletet and Hautefeuille have just demonstrated for a single pressure, namely, that the continuity of the gaseous and liquid states enunciated by Andrews is only apparent.

J. W.

**Retrogradation produced by the Electric Discharge during the Conversion of Oxygen into Ozone.** By P. HAUTEFEUILLE and J. CHAPPUIS (*Compt. rend.*, 94, 646—649).—When oxygen is subjected to the action of the electrical discharge at a pressure below 50 mm., the ozone produced is alternately decomposed and reformed. The same phenomenon is observed when the discharge acts on a mixture of oxygen with silicon fluoride. It is not due to any alteration in the nature of the discharge caused by the formation of ozone, or by the reduction of pressure which accompanies the conversion of oxygen into ozone. The real cause is development of heat. The same phenomenon can be brought about at pressures lower than that at which it is usually observed (between 50 and 100 mm.), by increasing the rapidity of discharge, so that the oxygen cannot be maintained at the initial temperature. Under these pressures, however, the oscillations are less regular than in the first case, and depend on the pressure, the temperature, and the length of spark given by the coil. A short interruption of the discharge during a phase of transformation of ozone into oxygen only temporarily interrupts the destruction of the former, for, on continuing the discharge, the destruction also continues. If, however, the interval exceeds a minute, then on recommencing the discharge, the amount of ozone increases. This is

probably due to the fact that the cold walls of the apparatus do not instantly bring the gas to its initial temperature. Further, the presence of a gas, such as hydrogen, which is a good conductor of heat, prevents this rapid and intermittent destruction of ozone under low pressures.

It would appear that ozone is less stable during the passage of the discharge the lower the pressure, but the authors intend to make further experiments on this point.

C. H. B.

**Researches on Chemical Equivalence. I. Manganous and Nickelous Sulphates.** By E. J. MILLS and J. H. BICKET (*Phil. Mag.* [5], 13, 169—177).—The object of this investigation was to determine on what terms manganous and nickelous sulphates were mutually equivalent, the particular equivalence examined being equivalent precipitability of the sulphates by sodium carbonate, from an aqueous solution. The conclusions arrived at were as follows:—(1.) Precipitability is a linear function of mass. (2.) When a mixture of the sulphates of manganese and nickel is precipitated by sodium carbonate, equal weights of them are equally precipitable, the attraction of one of them for the reagent being the inverse of that of the other. (3.) When the above sulphates are separately precipitated by the same reagent, they are equally precipitable, and do not exhibit the inverse function. (4.) It is probable that the precipitabilities of the commixed and separate sulphates are mathematically related in a simple manner. (5.) Within moderate limits, precipitation does not appear to be affected by temperature.

T. C.

**Researches on Chemical Equivalence. II. Nickel and Cadmium Sulphates.** By E. J. MILLS and B. HUNT (*Phil. Mag.* [5], 13, 177—179).—As a result of their experiments, the authors conclude that the sulphates of nickel and cadmium are not comparable in point of precipitability, and that two elements belong to the same group when, in saline solutions of identical genus, they may be equally precipitable. This latter statement, however, requires confirmation in the case of reagents other than sodium carbonate, which was the precipitant employed in the research.

T. C.

**Lecture Experiments.** By V. MEYER (*Ber.*, 15, 297—298).—In order to demonstrate the blue colour of pure water, the author unites five glass tubes of about 40 mm. in diameter, and  $1\frac{1}{2}$  m. long, by means of short pieces of caoutchouc tube, so as to form one tube of  $7\frac{1}{2}$  m. long. This tube is placed in a horizontal position, and surrounded with a black cloth. On filling the tube with distilled water, an intense blue field is apparent to an observer looking through the tube.

In order to show the conversion of yellow into red phosphorus by heating the former above its boiling point in a sealed tube, the author heats the tube in a bath of diphenylamine vapour in his vapour-density apparatus.

V. H. V.

**Lecture Experiments.** By M. ROSENFELD (*Ber.*, **15**, 160—162).—*Decomposition of Steam by Red-hot Iron or Magnesium in a Glass Tube.*—3 to 4 grams of finely-divided iron are put into a piece of combustion-tube, 12 to 13 cm. long, by 14 mm. diameter, connected at one end with a flask containing 10 to 15 c.c. hot water, and at the other end with a gas-delivery tube. The tube is inclined upwards from the flask. To use it, the tube is strongly heated and the water gently boiled; a regular and copious evolution of hydrogen takes place. If magnesium ribbon is used instead of iron, then the tube is heated until the metal begins to melt and burn, and the current of steam is sent through very quickly; the magnesium burns with an intense light, and hydrogen is given off abundantly.

*Burning Ammonia in Oxygen* (see this vol., 138).—The drying tube should be moderately large to insure easy ignition, and if in course of the experiment the flame goes out, this tube should be refilled with soda-lime. With excess of ammonia, the flame is luminous and round; with excess of oxygen, the flame is less luminous and pointed. It is this flame which melts platinum, and makes lime glow.

D. A. L.

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## Inorganic Chemistry.

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**Transformation of Ozone into Oxygen by Heat.** By IRA REMSEN (*Amer. Chem. J.*, **4**, 50—53).—The molecule of ordinary oxygen is supposed to contain 2, and that of ozone 3 atoms of oxygen. If this be the case, the conversion of ozone into oxygen may be supposed to take place by the splitting up of 2 mols.  $O_3$  into 6 atoms of free oxygen, and the rearrangement of these into 3 mols.  $O_2$ ; and, granting this, it seems probable that, in the conversion of ozone into ordinary oxygen, which may be effected by heat, there must be a moment when the oxygen-atoms will exist in the free state, and may therefore be expected to exhibit peculiarly active properties. Now, ozone does not oxidise carbon monoxide to the dioxide, whereas this change is known to be effected by the nascent oxygen produced by the action of palladium-hydrogen on ordinary oxygen; and it may therefore be expected that if the conversion of ozone into oxygen be made to take place in presence of carbon monoxide, then, if the above-mentioned view of the mode of this conversion be correct, there must arrive a moment at which the oxygen-atoms, being in the uncombined state, will be able to effect it. To test the correctness of this view, a mixture of pure carbon monoxide and highly ozonised oxygen was passed through a U-tube, and thence through clean lime-water, and the U-tube was gradually heated to about  $300^\circ$ . Under these conditions, the current of gas was continued for an hour, but no *precipitate was formed in the lime-water*. Hence it appears that no carbon dioxide was produced, and consequently the experiments afford no proof that the oxygen, in passing from the state of ozone to its ordinary state,

exhibits at any moment the peculiarly active properties of nascent oxygen. H. W.

**Active Oxygen.** By E. BAUMANN (*Zeits. Physiol. Chem.*, 5, 244—257).—The author believes that, in addition to ozone and the ordinary inactive form of oxygen, there exists yet another modification—active or nascent oxygen—which, like nascent hydrogen, does not admit of isolation, and can only be examined through its action on other bodies. This active oxygen (O) is the most powerful oxidising agent known, and is in a state to combine with inactive oxygen (O<sub>2</sub>), in order to form ozone (O<sub>3</sub>). In its action it differs from ozone, in that it is capable of converting water into hydrogen peroxide, and the nitrogen of the air into nitrous and nitric acid, which ozone does not. The author adduces a new difference. If a mixture of ozonised air and carbonic oxide be passed through baryta-water, no turbidity is produced; carbonic oxide cannot be converted into carbonic anhydride by this means. This result agrees with those of Remsen and Southworth. If, however, palladium foil saturated with hydrogen, be enclosed in a glass tube with clean lime-water, oxygen, and carbonic oxide, a turbidity is slowly produced, owing to the formation of calcic carbonate. The active oxygen, developed under these circumstances, possesses a power which ozone does not. The author then points out the importance of Hoppe-Seyler's work on the part played by active oxygen, for the comprehension of the oxidations which take place in the organism. The rest of the paper is devoted to a criticism of Nencki's work. W. N.

**Formation of Hydrogen Peroxide during Combustion.** By A. SCHULLER (*Ann. Phys. Chem.* [2], 15, 289—292).—When oxygen is burnt in hydrogen, the ordinary small flame is accompanied by a second and much larger blue flame, the nearer investigation of which showed that under these circumstances hydrogen peroxide is produced. The appearance of the larger flame is not observed when hydrogen is burnt in oxygen, but is rendered still more evident if a little sulphurous anhydride be added to the gas, and disappears altogether when the gases are previously passed through caustic potash. The larger blue flame, therefore, is due to the presence of sulphurous anhydride. The water produced by the combustion contains traces of sulphuric acid, when the large blue flame is observed, but otherwise it cannot be detected. The water *always* contains hydrogen peroxide, which is produced no matter whether the hydrogen is burnt in oxygen or the oxygen in hydrogen, although the quantity produced in the two cases is very different. The greater the rate at which the burning gas is pressed into the flame, the greater the quantity of hydrogen peroxide formed. In one case, when oxygen was burnt in hydrogen, 1 gram of the water formed contained 0·0008 gram of H<sub>2</sub>O<sub>2</sub>. The presence of sulphurous anhydride hinders the formation of hydrogen peroxide, whilst it is one of the conditions of the formation of the blue flame referred to above; it presumably reduces an equivalent quantity of H<sub>2</sub>O<sub>2</sub> to H<sub>2</sub>O with formation of sulphuric acid.

An explosion of a mixture of hydrogen and oxygen appears to give

rise to a still greater quantity of hydrogen peroxide than ordinary combustion.

The above facts would account for the green edge which the hydrogen flame exhibits in presence of iodine, the simultaneous formation of iodic acid observed by Salet (*Compt. rend.*, **80**, 884) being probably due to the presence of hydrogen peroxide. T. C.

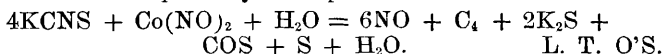
**Carbonic Anhydride in the Atmosphere.** By DUMAS (*Compt. rend.*, **94**, 589—594).—A review of past and recent investigations on the amount of carbonic anhydride in the atmosphere, in which the author lays special stress on its constancy. He points out the importance of making observations in different parts of the world with a view to determine the variations in the proportion of carbonic anhydride caused by great atmospheric movements. He considers that the quantity of carbonic anhydride produced by combustion and the respiration of animals, and the quantity removed by the action of plants cannot be compared in point of magnitude with that derived from subterranean sources, and that removed as calcium carbonate and deposited at the bottom of the sea.

When air is passed over potash, if the latter contains organic matter, it will absorb oxygen in addition to carbonic anhydride, and if pumice-stone saturated with it contains ferrous oxide, the latter will also absorb oxygen. C. H. B.

**Combination of Carbonic Acid and Water.** By S. WROBLEWSKI (*Compt. rend.*, **94**, 212—213).—From certain phenomena observed in a tube in which carbonic acid gas is compressed in presence of water, the author infers the existence of a definite but readily dissociable hydrate capable of existing only under certain pressures increasing with the temperature, and equal to 12·3 atmospheres at 0°.

R. R.

**Preparation of Nitric Oxide.** By D. E. JOHNSTONE (*Chem. News*, **45**, 159).—Nitric oxide may be readily prepared in large quantities by heating together 4 parts potassium thiocyanate and 1 part cobalt nitrate, either in solution, or in the solid state slightly moistened with water. The reaction probably takes place as follows:—



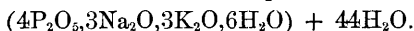
L. T. O'S.

**Saturation of Phosphoric Acid by Bases.** By A. JOLY (*Compt. rend.*, **94**, 529—531).—The author has employed "methyl-orange" and "helianthine" as indicators instead of litmus, and finds that 1 equivalent of phosphoric acid is perfectly neutralised by 1 equivalent of an alkali (potash, soda, or ammonia). Solutions of phosphates containing only 1 equivalent of base, which strongly redden litmus, are neutral to helianthine. Hence it would appear that the first equivalent of alkali behaves with phosphoric acid exactly as with a true monobasic acid. This confirms the conclusion drawn by Berthelot and Louguinine from their thermochemical experiments (*Ann. Chim. Phys.* [5], **8**, 53).

C. H. B.

**Phosphates Neutral to Litmus.** By E. FILHOL and SENDERENS (*Compt. rend.*, **94**, 649—650).—Sodium hydroxide is very cautiously added to a solution of phosphoric acid until the liquid is exactly neutral to litmus; it is then evaporated, first at a gentle heat, afterwards over sulphuric acid in a vacuum. In this way, oblique rhombic prisms are obtained, which contain 3 mols.  $\text{H}_2\text{O}$ , and are neutral to litmus; this salt may be regarded as a combination of 1 mol. monosodium phosphate with 1 mol. disodium phosphate. It loses its water of crystallisation at  $110^\circ$ , without melting, and its water of constitution at  $200^\circ$ . At a higher temperature it melts, and, on cooling, solidifies to a transparent vitreous mass. When a solution of the salt is concentrated in a current of dry air at the ordinary temperature, crystals are obtained which contain 15 mols.  $\text{H}_2\text{O}$ , melt in their water of crystallisation at  $55^\circ$ , and lose the whole of their water at  $200^\circ$ . In order to obtain this salt, it is essential that the solution be exactly neutral; the least excess of either acid or base causes the separation of alkaline disodium phosphate from an acid mother-liquor.

The author was unable to obtain the corresponding potassium and ammonium compounds. The double sodium and potassium salt forms monoclinic prismatic needles of the composition



The ammonium salt contains only 6 mols. water of crystallisation, and readily splits up in presence of water into a mixture of mono- and di-phosphate.

C. H. B.

**Phosphorus Pentasulphide.** By H. GOLDSCHMIDT (*Ber.*, **15**, 303—304).—By means of the air thermometer which the author, in conjunction with V. Meyer, has recently described (*Ber.*, **15**, 137), the author has determined the boiling point of phosphorus pentasulphide. One preparation boiled at  $519^\circ$  at a pressure of 734 mm., and a second at  $517^\circ$  at a pressure of 728.5 mm., mean  $518^\circ$ . This value differs from that ( $550^\circ$ ) obtained in former determinations. This difference the author considers to be due to impurities consisting of higher boiling sulphides of phosphorus, which were rigorously excluded in his present experiments.

V. H. V.

**Note on the Action of Sulphuric Acid on Zinc and on Tin.** By M. M. P. MUIR and C. E. ROBBS (*Chem. News*, **45**, 69—71).—The tabulated qualitative experiments show that strong sulphuric acid,  $7\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$ , exerts no action on zinc until a high temperature is reached, and that the gaseous product of the action which then occurs is sulphurous anhydride, accompanied by separation of a little sulphur;  $7\text{H}_2\text{SO}_4, 4\text{H}_2\text{O}$  acts in a similar manner, but more sulphur separates; with  $7\text{H}_2\text{SO}_4, 6\text{H}_2\text{O}$ , sulphurous anhydride is no longer produced, but only sulphuretted hydrogen and sulphur; as the acid is made more dilute, the action commences at lower temperatures, with evolution of hydrogen and traces of sulphuretted hydrogen, or of hydrogen alone; the quantity of sulphuretted hydrogen is increased by rise of temperature, but it is not accompanied by sulphurous anhydride or sulphur. Strong sulphuric acid begins to act on tin at ordinary temperatures, but the amount of action is very small; the

products are sulphurous anhydride with a slight separation of sulphur. As the temperature rises the quantities increase, and a little sulphuretted hydrogen begins to appear. With a more dilute acid (1 : 1) this latter gas comes off at a lower temperature, whilst at about 120°, hydrogen, sulphuretted hydrogen, and sulphurous anhydride are simultaneously formed, and sulphur separates. More dilute acids have little or no action until the temperature approaches the boiling points of the acids, when the gaseous products are hydrogen and sulphuretted hydrogen, or in the case of  $\text{H}_2\text{SO}_4 : 7\text{H}_2\text{O}$ , hydrogen only, no sulphur being formed with this acid. The bearing of these experiments on the supposed mode of action is discussed.

H. B.

**Density of the Vapour of Pyrosulphuryl Chloride.** By J. OGIER (*Compt. rend.*, **94**, 217—220).—The author has carefully re-determined the density of the vapour of pyrosulphuryl chloride at temperatures below 200°, his results giving the number 3.72. Although this is half the theoretical density of the compound  $\text{S}_2\text{O}_5\text{Cl}_2$ , the author does not admit that any dissociation takes place within the range of temperature employed in his experiments.

R. R.

**A New Sulphur Oxychloride.** By J. OGIER (*Compt. rend.*, **94**, 446—448).—Equal weights of sulphur chloride and sulphuryl chloride are heated at 250° in strong sealed tubes for several hours. On opening the tubes, sulphurous anhydride is evolved in considerable quantity, and on distillation, the product yields a deep red liquid of lower boiling point than the two known oxychlorides, together with the excess of sulphur chloride, which contains dissolved sulphur. The red compound has the composition  $\text{S}_2\text{OCl}_4$ , and is formed in accordance with the equation  $2\text{S}_2\text{Cl}_2 + 2\text{SO}_2\text{Cl}_2 = 2\text{S}_2\text{OCl}_4 + \text{SO}_2 + \text{S}$ . It is also obtained, although with greater difficulty, by heating sulphur chloride at 250° with thionyl chloride saturated with chlorine, thus:  $\text{S}_2\text{Cl}_2 + \text{Cl}_2 + 2\text{SOCl}_2 = 2\text{S}_2\text{OCl}_4$ . The compound  $\text{S}_2\text{OCl}_4$ , is a deep red liquid, with an odour resembling that of sulphur chloride, but more penetrating; b. p. 60—61°; sp. gr. at 0° = 1.656. It is decomposed by water, with precipitation of sulphur, part of which is insoluble in carbon bisulphide, and formation of hydrochloric, sulphuric, and sulphurous acids, together with a notable quantity of thionic acids. When heated, it decomposes, even below 100°, into sulphur chloride, chlorine, and sulphurous anhydride, a portion of which recombines on cooling. This dissociation prevents the accurate determination of the vapour-density of the compound. Experiments at low temperatures gave as a mean result 3.87. The oxychloride reacts violently with absolute alcohol; hydrochloric acid, ethyl chloride, and sulphurous anhydride being evolved. The colourless liquid formed remains clear, but on distillation excess of alcohol first passes over, then a large quantity of sulphur is precipitated, and finally normal ethyl sulphite distils over at about 150°. Precipitation of sulphur is also caused by addition of a trace of water to the clear liquid. Possibly the alcoholic liquid contains an ether of an acid derived from  $\text{S}_2\text{O}_3$ , the oxychloride being formed from  $\text{S}_2\text{O}_3$  by the substitution of  $\text{Cl}_4$  for  $\text{O}_2$ .

C. H. B.



**Action of Litharge on the Iodides of the Alkali-metals.** By A. DITTE (*Compt. rend.*, **92**, 1454—1457).—Plumbous hydroxide is immediately attacked when treated with a solution of potassium iodide in a closed vessel, and is transformed into the oxyiodide  $2(\text{PbI}_2, \text{PbO}) + \text{H}_2\text{O}$ , which can be obtained in a well crystallised condition. If, however, the operation is carried on in open vessels, the carbonic anhydride in the air takes part in the reaction. Carbonate of lead is not attacked by iodide of potassium at the ordinary temperature, even when it is in excess, but in presence of free carbonic acid, which dissolves the carbonate, the compound  $\text{PbI}_2, 2\text{KI} + 4\text{H}_2\text{O}$  is obtained, crystallised in beautiful white needles. These reactions are quite in accordance with the thermic law of maximum work. T. C.

**Influence of the Concentration of Hydrochloric Acid on the Solubility of Silver Chloride.** By F. RUYSSSEN and E. VARENNE (*Compt. rend.*, **92**, 1459—1461).—As stated in an earlier communication (*ibid.*, **92**, 1161) the solubility of chloride of silver increases with the concentration of the silver nitrate solution with which it is precipitated, but without showing any clearly marked regularity. The authors now find that other sparingly soluble chlorides, viz., mercurous chloride and lead chloride, also show a similar behaviour, and that the solubility of the silver chloride likewise increases with the concentration of the hydrochloric acid. T. C.

**Basic Calcium Carbonate.** By F. M. RAOULT (*Compt. rend.*, **92**, 1457—1459).—Basic calcium carbonate,  $\text{CaCO}_3, \text{CaO}$ , is obtained when freshly burnt lime is heated in a current of carbonic anhydride. The lime glows strongly during the operation. That this basic carbonate is not a mixture of neutral carbonate and free lime is shown by the fact that it does not disintegrate on exposure to moist air, nor does it take up water when treated with dry steam at  $200^\circ$ . When finely powdered and treated with a small quantity of water, or even under water, it hardens like hydraulic cement, without any sensible evolution of heat. The hydrated product has the formula  $\text{CaCO}_3, \text{Ca}(\text{HO})_2$ , and when reduced to a powder and treated with water, it gradually loses all the lime which it cannot retain in the form of neutral carbonate. The hydrate loses water at a dull red heat, and is converted into a mixture of calcium carbonate and oxide. The same amount of heat (54.4 cal.) is evolved when the basic carbonate  $\text{CaCO}_3, \text{CaO}$  is dissolved in nitric acid as when 2 mols.  $\text{CaCO}_3$  are dissolved therein.

The basic salt,  $2\text{CaCO}_3, \text{CaO}$ , is obtained when burnt lime is heated for several days in contact with carbonic anhydride; when powdered and treated with water, it behaves like the preceding compound.

T. C.

**Preparation of Calcium Hypophosphite.** By F. W. SHORT (*Pharm. J. Trans.* [3], **12**, 824).—Rose has shown (*Pogg. Ann.*, **12**, 297) that when calcium hypophosphite is boiled with calcium hydroxide, hydrogen is evolved, and calcium phosphate formed. The author has repeated this reaction, which probably takes place as follows:— $\text{Ca}_2\text{P}_2\text{H}_2\text{O}_2 + 2\text{Ca}(\text{HO})_2 = \text{Ca}_3\text{P}_2\text{O}_4 + 4\text{H}_2$ . It is owing to this reaction that calcium phosphate is formed when phosphorus is boiled

with excess of calcium hydroxide. By boiling calcium hypophosphite with phosphorus, only small quantities of calcium phosphate are formed, with no appreciable evolution of gas. L. T. O'S.

**Action of Sulphur on Glass.** By W. SELEZNEFF (*Jour. Russ. Chem. Soc.*, 1882, 124—130).—In the years 1877—79, Ebel published the result of his researches on the existence of a normal glass. He fused different kinds of glass with sulphur, and states that the "normal glass" contains 2.5 silica for 1 of alkali, as only those glasses are coloured yellow or brown on fusion with sulphur, which contain more alkali than corresponds with the above proportions, the sulphur having acted on the excess of free alkali.

The author repeated Ebel's experiments with different kinds of glass, ordinary and "soluble," containing from 1.5 to 3 of  $\text{SiO}_2$  for 1 of alkali. In all cases a coloration took place, and was the darker the more alkaline was the glass. On treating the glass with acids, sulphuretted hydrogen was set free, the quantity of which diminished with the dark colour of the glass. This proves that the glass contains polysulphides of alkali-metals, but only when the fusion was carried on in covered crucibles. If the crucibles are uncovered, the sulphur burns away. The author's experiments contradict Peligot's views, according to which the dark colour of such glass is due to the presence of a dark modification of sulphur.

In presence of water, all alkaline silicates are decomposed with formation of alkaline polysulphides. This is the case even with ordinary glass (*e.g.*, of the composition  $\text{Na}_2\text{O}, \text{CaO}, 6\text{SiO}_2$ ) when boiled in fine powder with water and flowers of sulphur. In this case, the glass is first decomposed by water into an alkaline silicate, which is then acted on by the sulphur. All these experiments contradict Ebel's views on the existence of a normal glass, stable at all temperatures, and even in presence of water.

The author moreover acted on powdered glass with sulphur, at a temperature of  $500^\circ$ , in sealed tubes. The glass was completely decomposed, free silica and alkaline sulphides being formed. From glass of the composition  $6\text{SiO}_2, \text{CaO}$  (or  $\text{PbO}$ ),  $\text{K}_2\text{O}$  (or  $\text{Na}_2\text{O}$ ) sulphur extracted from 13.5—21.5 of alkali. B. B.

**Magnesium Oxychlorides.** By G. ANDRÉ (*Compt. rend.*, 94, 444—446).—20 grams calcined magnesia were boiled with a solution of 400 grams magnesium chloride in 500 grams water, and the solution filtered. After some time the filtrate deposited a precipitate apparently amorphous but really consisting of white microscopic needles,  $\text{MgCl}_2, \text{MgO} + 16\text{H}_2\text{O}$ . The heat of formation of the compound was determined by dissolving it in dilute hydrochloric acid, and measuring the heat developed,  $\text{MgCl}_2 + \text{MgO}$  (hydrated)  $+ 16\text{H}_2\text{O} = \text{MgCl}_2, \text{MgO} + 16\text{H}_2\text{O}$ , develops  $+ 42.36$  cals. ( $\text{H}_2\text{O}$  liquid),  $+ 19.78$  cals. ( $\text{H}_2\text{O}$  solid). When dried in a vacuum until it ceases to lose weight, this compound is converted into the oxychloride  $\text{MgCl}_2, \text{MgO} + 6\text{H}_2\text{O}$ , the heat of formation of which  $= + 33.76$  cals. ( $\text{H}_2\text{O}$  liquid) or  $+ 25.18$  cals. ( $\text{H}_2\text{O}$  solid). The combination of  $10\text{H}_2\text{O}$  with this hydrate, therefore, develops  $+ 8.6$  cals., and the combination

of  $\text{MgO}$  with  $\text{MgCl}_2 + 6\text{H}_2\text{O}$ , crystallised, develops + 9.56 cals. Both oxychlorides are at once decomposed by water and alcohol.

The oxychloride obtained by heating calcined magnesia with a solution of magnesium chloride (Krause, *Annalen*, **165**, 38), forms microscopic crystals, and when dried in a vacuum, has the composition  $\text{MgCl}_2, 10\text{MgO} + 16\text{H}_2\text{O}$ . The formation of this compound from anhydrous magnesium chloride and hydrated magnesia develops + 33 cals. ( $\text{H}_2\text{O}$  liquid), or + 10.2 cals. ( $\text{H}_2\text{O}$  solid). When dried at  $120^\circ$ , this hydrate is converted into  $\text{MgCl}_2, 10\text{MgO} + 13\text{H}_2\text{O}$ , the heat of formation of which = + 28.6 cals. ( $\text{H}_2\text{O}$  liquid), or + 10 cals. ( $\text{H}_2\text{O}$  solid). The combination with the last  $3\text{H}_2\text{O}$ , therefore, develops + 4.4 cals. ( $\text{H}_2\text{O}$  liquid). Dried over sodium hydroxide, the oxychloride has the composition  $\text{MgCl}_2, 10\text{MgO} + 18\text{H}_2\text{O}$ , the heat of formation of which = + 36.8 cals. ( $\text{H}_2\text{O}$  liquid).

When 1 equivalent anhydrous magnesium oxide is fused with 1 and 2 equivalents respectively of anhydrous magnesium chloride, deliquescent friable compounds are obtained, which are decomposed by dilute hydrochloric and sulphuric acids, but the magnesia dissolves only very slowly. The heat of formation of  $\text{MgO}, 2\text{MgCl}_2$  is + 19 cals., that of  $\text{MgO}, \text{MgCl}_2$  + 18.4 cals.

C. H. B.

**Boiling Point of Zinc.** By J. VIOLLE (*Compt. rend.*, **94**, 720—722).—The boiling point of pure zinc is  $930^\circ$ , a number which agrees closely with that given by Becquerel,  $932^\circ$ ; but differs considerably from that given by Deville and Troost,  $1040^\circ$ . The determination was made in an apparatus specially constructed to prevent cooling by radiation, &c.

C. H. B.

**Composition of the Crystals deposited on the Zincs in Leclanché's Battery.** By A. LONGI (*Gazzetta*, 1881, 514—516).—These crystals were regarded by Prioznik as zinc ammonium chloride,  $\text{N}_2\text{H}_6\text{ZnCl}_2$ , and by Divers as a compound of zinc hydroxide with sal-ammoniac,  $\text{Zn}(\text{OH})_2, \text{NH}_4\text{Cl}$ . Longi has arrived at a very different result. He examined crystals deposited on the zinc of a Leclanché battery which had been in action for a year, and found them to be rhombic dodecahedrons, containing only 0.62 per cent. of zinc. On dissolving them in water, and leaving the solution to evaporate, crystals of pure ammonium chloride were obtained, having the usual form of octohedrons grouped in plumose tufts. It is remarkable that the small quantity of zinc contained in the original crystals should have caused them to assume the dodecahedral form, which is never found in pure sal-ammoniac crystallised from aqueous solution, but is often observed by the crystals of that salt in volcanic regions, as found by Silvestri in the fumaroles of Etna, and by others on Vesuvius.

H. W.

**Further Notes on Actinium and on the Equivalent of Zinc.** By T. L. PHIPSON (*Chem. News*, **45**, 61).—The oxide has not yet been obtained free from zinc oxide. The purified zinc oxide obtained in a crystalline state from the soda-solutions has served for new determinations of the equivalent of zinc; this appears to be a whole number, viz., 32. A sulphide of actinium has been obtained, which is only

slightly sensitive to the action of light; the darkening of the ordinary form of the sulphide is prevented by the interposition of either white or blue glass of 2 mm. thickness. H. B.

**Gallium Oxychloride.** By L. DE BOISBAUDRAN (*Compt. rend.*, **94**, 695—697).—A specimen of hydrated gallium chloride, prepared in 1878, and enclosed in a sealed tube, remained unaltered for some time, but was found in 1881 to have changed to a mass of small crystals, surrounded by a liquid which had a strongly acid reaction. The crystals are small octohedrons with truncated angles, and without action on polarised light. They are only slightly soluble in water or nitric acid, but dissolve slowly in hydrochloric acid, and immediately in potash. Analysis leads to the formula  $\text{Ga}_6\text{O}_6\text{Cl}_6 + 14\text{H}_2\text{O}$ , or  $\text{Ga}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O} + 2(\text{Ga}_2\text{O}_3, \text{H}_2\text{O})$ , a compound of a molecule of a hydrated chloride corresponding with aluminium chloride, with two molecules of a hydrated oxide corresponding with aluminium monohydrate.

C. H. B.

**Aluminium Sulphates.** By S. U. PICKERING (*Chem. News*, **45**, 121—122, 133—135, 146—147).—Nine basic sulphates of aluminums have been described, and the following research was undertaken with the object of proving the existence or non-existence of such compounds. Owing to the difficulty with which aluminium sulphate is obtained free from potassium, it was necessary to concentrate a solution of the commercial substance until it partially crystallises, and filter off the remaining solution, which was found to contain the base and acid in the proportion required by the formula  $\text{Al}_2\text{SO}_4$ , and only very small traces of potassium. On washing the basic sulphates with water, they undergo slight decomposition, but, unlike the ferric sulphates, a portion of the base as well as the acid is dissolved in the ratio of about 20 to 80. Owing to the great difficulty attending the drying of the precipitates, they were analysed in the wet state without weighing, the ratio of alumina to sulphuric anhydride only being estimated.

*Precipitation with Sodium Carbonate.*—When varying quantities of aluminium sulphate are treated with varying amounts of sodium carbonate, no definite basic sulphate is precipitated. At first the basicity of the precipitate decreases gradually, and afterwards continues to increase until it consists of pure alumina. The composition of the precipitates varies both with the amount of alkali added and the quantity of water present. The composition of the least basic of the precipitates indicates a body varying between  $3\text{Al}_2\text{O}_3, 2\text{SO}_3$ , 65·69 per cent.  $\text{Al}_2\text{O}_3$ , and  $5\text{Al}_2\text{O}_3, 3\text{SO}_3 = 68\cdot02$  per cent.  $\text{Al}_2\text{O}_3$ , or  $2\text{Al}_2\text{O}_3, \text{SO}_3 = 71\cdot85$  per cent.  $\text{Al}_2\text{O}_3$ .

*Precipitation with Ammonia.*—On adding increasing quantities of ammonia to aluminium sulphate, and filtering the precipitate after standing a few minutes, the basicity of the precipitate increases with the quantity of the alkali used, as is seen by Nos. 31—34 in the table. If, however, the precipitate is filtered as soon as it is formed, the opposite result is obtained (35—36). The solvent action of the alkaline solution on the precipitate is considerably diminished by increasing the amount of water present, and in this case results similar to

those with sodium carbonate are obtained; at first the basicity of the precipitate slightly diminishes, remaining constant during the precipitation of 45 per cent. alumina, after which it gradually increases until it consists of pure alumina.

TABLE I.—*Precipitation of Aluminium Sulphate with Ammonia.*

	Al <sub>2</sub> O <sub>3</sub> in precipitate. Ditto in solution, taken = 100.	Per cent. Al <sub>2</sub> O <sub>3</sub> in anhydrous precipitate.
31.....	9	71·324
32.....	53	74·44
33.....	92	89·939
34.....	100	98·835
35.....	13·1	76·328
36.....	16·4	74·14
37.....	5	71·116
38.....	21	69·494
39.....	21	67·17
40.....	24	67·345
41.....	22	68·519
42.....	7	90·86

These results, therefore, disprove Maw's statement (*Pogg. Ann.*, **11**, 80) that a basic sulphate of the composition Al<sub>2</sub>O<sub>3</sub>.SO<sub>3</sub> is obtained on adding an alkali to the normal sulphate; they do not even tend to show that the precipitates formed are definite compounds.

*Solution of Aluminium Hydrate and Basic Sulphate by Normal Sulphate.*—On adding aluminium hydroxide to boiling solutions of the normal sulphate varying in strength from 40 to 50 per cent. to 1 per cent. until the solution became cloudy, the basicity of the resulting solutions was found to increase with the strength of the sulphate solution, and in all cases to exceed that of the normal sulphate (which does not lose sulphuric acid on boiling with water), the percentage of Al<sub>2</sub>O<sub>3</sub> being from 34·83 to 33·532. Strongly ignited alumina is also dissolved by the boiling sulphate solution.

When a solution of normal sulphate is treated with basic sulphate containing 63 per cent. Al<sub>2</sub>O<sub>3</sub>, the resulting sulphate contains 52·984 per cent. Al<sub>2</sub>O<sub>3</sub>, considerably more basic than any obtained by the use of the hydrate, yet corresponding to no definite compound. On diluting the solution with small quantities of water, no precipitate is formed, but large quantities produce an abundant flocculent precipitate.

*Ignition of Ammonium Alum.*—Ammonium alum when heated loses first its water, then the ammonium sulphate, leaving anhydrous aluminium sulphate, which on further heating in small quantities until it no longer loses weight, leaves pure alumina. The heated sulphate continues to dissolve in water until it contains about 32 per cent. Al<sub>2</sub>O<sub>3</sub>, after which an insoluble portion is formed, which increases with the time of ignition. By partially decomposing the aluminium sulphate obtained from the decomposition of ammonium

alum, and dissolving the mass in water, Marguerite (*Compt. rend.*, **90**, 1354) obtained rhombohedrons either simple or terminating in four-sided pyramids of the composition  $\text{Al}_2\text{O}_3, 2\text{SO}_3$ . The author has obtained similar crystals which consist of potassium alum contained in the ammonium alum as an impurity. No confirmation of Marguerite's results could be obtained.

*Aluminium Sulphate and Zinc.*—When aluminium sulphate is treated with zinc at  $100^\circ$ , hydrogen is at first copiously evolved, but after from  $2\frac{1}{2}$  to 40 hours the reaction becomes very slow, and a cloudiness appears, which gradually increases and a precipitate forms; this, although not very dissimilar from that obtained by Debray (*Bull. Soc. Chim.* [2], **7**, 9) under similar circumstances in a platinum crucible, to which he gave the formula  $5\text{Al}_2\text{O}_3, 3\text{SO}_3$ , yet it cannot be considered as a definite compound, since its basicity increases with the dilution of the solution. The author's experiments were carried out in glass vessels, but when platinum vessels are used, the reactions appear to be the same, but proceed more rapidly, owing to the couple formed by the two metals.

By digesting aluminium sulphate with zinc in the cold, Debray obtained a jelly which, when washed, was found to contain 62.55 per cent.  $\text{Al}_2\text{O}_3$ . On repeating this experiment with solutions varying from 17—3.3 per cent. sulphate, a jelly separates out in each case, although decreasing in quantity, until below the latter strength no jelly was obtained, but a flocculent white precipitate. The jelly is dissolved by solution of normal sulphate, and is decomposed by water. Hence Debray's analysis must refer to the decomposed product. The analysis of the precipitate indicates a slight increase of basicity with increase in the strength of the solution. It is further dependent on the temperature with which it varies inversely. Although the amount of  $\text{Al}_2\text{O}_3$  (66.339—64.625 in 7 experiments) agrees fairly well with that required by the formula  $3\text{Al}_2\text{O}_3, 3\text{SO}_3 = 65.687$ , yet considering the influence of the strength of the solution and temperature, the author refrains from assuming that the precipitate has a constant composition.

*Decomposition of Basic Sulphates from Basic Solutions.*—The precipitates deposited from solutions of basic sulphates have no definite composition, and the crystals containing 49.86 per cent.  $\text{Al}_2\text{O}_3$ , obtained by Rammelsberg (*Pogg. Ann.*, **43**, 583), on keeping a basic solution of aluminium sulphate for several years, the author attributes to the presence of normal sulphate, since microscopic examination of the precipitates obtained by the author revealed no indication of crystalline structure.

*Basic Solutions Diluted with Water.*—On treating normal sulphate solutions with zinc, and diluting the clear solution until precipitates are formed, these precipitates increase in basicity with the quantity of zinc used, and consequently with the basicity of the solution. All attempts to prepare an acid aluminium sulphate were unsuccessful.

These results, considered as a whole, show that the so-called basic sulphates of aluminium have no definite composition, and that their composition varies continually with a variation in the physical conditions under which they are produced.

L. T. O'S.

**Atomic Weight of Glucinum as determined by its Physiological Action.** By G. BLAKE (*Chem. News*, 45, 111).—In spite of the many experiments that have been made to determine the atomic weight of glucinum, its true position among the elements is still undecided, as is shown by the conflicting views of a number of eminent chemists.

As the physical properties of the metal and its compounds have not so far furnished data to determine its true position amongst the elements, the author thinks the evidence derived from the physiological action of its salts may be of use in deciding this question. In 1840 he published the fact that the physiological action of inorganic substances when introduced directly into the blood of living animals, was determined by their isomorphous relations, all the substances in the same isomorphous group causing analogous physiological reactions. In 1870, it was shown that amongst the compounds of the more purely metallic elements in the same isomorphous group, the intensity of physiological action was determined by the atomic weight, the higher the atomic weight of an element in the different isomorphous groups, the smaller the quantity required to cause the same amount of physiological action. Applying these facts to the determination of the position of glucinum as a member of the magnesium or of the aluminium group of metals, it has to be ascertained whether its salts, when introduced directly into the blood of living animals, give rise to physiological reactions analogous to those characterising the salts of the magnesium group, or such as are produced by introducing the salts of alumina and ferric oxide, and whether the quantity required to produce these reactions is in proportion to the atomic weight of the substance, considered as a member of one or other of these isomorphous groups. The author found that the effects produced by the introduction of the salts of glucinum into the blood are the same as those caused by the salts of alumina and ferric oxide, and are strikingly different from the physiological reactions caused by the salts of the magnesium group. Again, the quantity required to produce these reactions agrees perfectly with its atomic weight as a member of the aluminium group. After performing some hundreds of experiments in ascertaining the physiological action of compounds of more than forty of the elements, the author considers the evidence furnished by the physiological action of the salts of glucinum to be decisive as to its position as a member of the aluminium group of metals.

D. B.

**Molybdenum Dioxide.** By F. MUNRO and R. R. PANEBIANCO (*Gazzetta*, 1881, 501—506).—To obtain measurable crystals of this oxide, the authors heated 14.4 g. molybdic trioxide with 14 g. dry potassium carbonate and 7 g. boric oxide, these numbers being in the proportion  $K_2O : MoO_3 : B_2O_3$ . The heat is kept up for three or four hours. The crucible is left to cool in the furnace, and the crystals disseminated through the fused mass are separated by washing it successively with ammonia, water, hydrochloric acid, and finally with water again. A strong heat is required, as at low temperatures only a few crystals are obtained in the midst of a reddish fused mass.

resembling ferric oxide, and apparently consisting of the hydrated dioxide.

The crystals, which are from 1 to 3 mm. long and 0.05 to 0.25 mm. thick, belong to the dimetric or quadratic system, having the axes  $a : c = 1 : 0.5774$ . Observed combinations  $\infty P.P$ ;  $\infty P.P\infty$ ;  $\infty P.P.\frac{1}{2}P\frac{1}{2}$ ;  $\infty P.\frac{1}{2}P\frac{1}{2}.P\infty.P$ ; and others of greater complexity. The crystals are opaque even in the thinnest laminæ; they have a metallic to adamantine lustre, copper-red to lead-grey colour, and sp. gr. = 6.44 at 16°.

Molybdenum dioxide is a member of the isomorphous group including the dioxides of tin, titanium, zirconium, and ruthenium. 100 parts of it yield, by oxidation, on the average, 112.44 parts  $MoO_3$ , a result which the authors regard as showing that the atomic weight of molybdenum is 96 and not 92. H. W.

**Silicomolybdic Acid.** By F. PARMENTIER (*Compt. rend.*, **94**, 213—215).—The author has succeeded in isolating silicomolybdic acid, in the form of large and brilliant yellow transparent crystals. In colour, crystalline form, and the mode of preparation of some of its salts, this substance is analogous to phosphomolybdic acid. Both these acids precipitate salts of thallium, mercurous salts, alkaloids, and compound ammonias. They also precipitate salts of rubidium and cæsium, and silicomolybdic acid is the most sensitive test for these elements in the presence of other alkali-metals. The formula for this acid is  $SiO_2.12MoO_3 + 13H_2O$ , corresponding with that of Marignac's silicotungstic acid. R. R.

**Action of Arsenic and Phosphoric Acids on the Sodium Salts of Tungstic Acid.** By J. LEFORT (*Compt. rend.*, **92**, 1461—1463).—A white semi-solid, amorphous, and very soluble precipitate, having the composition  $As_2O_5.3WO_3.3Na_2O.20H_2O$ , is obtained when a very concentrated cold solution of one part of arsenic acid is mixed with a similar solution of four parts of neutral sodium tungstate. If, however, one part of arsenic acid be mixed with two parts of sodium ditungstate, and the solution evaporated, a new metatungstic acid is obtained, crystallising with 7 mols.  $H_2O$ , in very fine yellow leaflets. To this acid, the name *metaluteotungstic acid* is given; it is also obtained if phosphoric acid is used instead of arsenic acid. The tungstic acid was determined by precipitation with acid quinine acetate and ignition of the precipitate. T. C.

**Researches on the Complex Inorganic Acids.** By W. GIBBS (*Chem. News*, **45**, 29—31, 50—52, 60—61).—*Phosphomolybdates*.—Analytical methods; the phosphoric and molybdic acids were precipitated together from the boiling solution by mercurous nitrate with addition of mercuric oxide. After burning the filter-paper with due precaution, a known quantity of normal sodium tungstate is added, and the mixture gradually raised to fusion. The sum of the two oxides is thus found; the phosphoric acid is afterwards determined, and the molybdic acid found by difference. If the phosphoric acid be precipitated with magnesia mixture and reprecipitated, there remains a mean error of 0.65 per cent. of the phosphoric acid estimated. The



precipitated double phosphate may be better purified by solution in hot dilute acid, and reprecipitation with ammonium sulphide, the precipitate being then boiled once or twice with more ammonium sulphide. For the estimation of water, it is often necessary to add sodium tungstate to prevent volatilisation of molybdic acid.

*Twenty-four Atom Series.*—Precautions to be observed in preparing the *octohedral hydrated acid* are given. The analyses of this body gave the ratio  $24\text{MoO}_3, \text{P}_2\text{O}_5$  with  $62\text{H}_2\text{O}$ ; but considering previous analyses by Finkener and Debray, the syrupy nature of the mother-liquor, and the constitution of phosphotungstic acid, the author holds it to contain 1 mol. water less. The ammonium salt, according to Finkener, contains always  $24\text{MoO}_3, \text{P}_2\text{O}_5$ , with varying percentages of water and ammonia; an analysis of such a compound is given; but there is also evidence that, as in the case of the phosphotungstates, there are series of phosphomolybdates in which the ratio of the molybdic to the phosphoric oxide is as 20 : 1, as 22 : 1, and as 24 : 1. Attempts were made to obtain well-defined salts with the cobaltamines, but only one crystalline salt was obtained, viz., by adding croceocobalt chloride to an acid solution of 7 : 3 ammonium molybdate and sodium phosphate. Its analysis gave the formula  $24\text{MoO}_3, \text{P}_2\text{O}_5, \text{CoO}, 2\text{H}_2\text{O} + 21 \text{Aq}$ , where  $\text{CoO} = \text{Co}_2(\text{NH}_3)_6(\text{NO}_2)_4\text{O}$ .

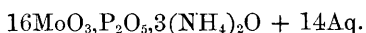
The potassium salt prepared similarly to the ammonium salt gave the formula  $24\text{MoO}_3, \text{P}_2\text{O}_5, 2\text{K}_2\text{O}, \text{H}_2\text{O} + 3\text{Aq}$ .

The *twenty-two atom series* has been partially examined by Rammelsberg, but not with very satisfactory results. Two analyses are given of the ammonium salt, which both give the formula  $22\text{MoO}_3, \text{P}_2\text{O}_5, 3(\text{NH}_4)_2\text{O} +$  an undetermined amount of water of crystallisation. An acid potassium salt was prepared and found to be  $22\text{MoO}_3, \text{P}_2\text{O}_5, 3\text{K}_2\text{O} + 22\text{MoO}_3, \text{P}_2\text{O}_5, 2\text{K}_2\text{O}, \text{H}_2\text{O} + 21\text{Aq}$ .

*Twenty Atom Series.*—The only salt obtained is one of ammonium, resembling the previous ones in appearance and formation. Its analysis gave  $60\text{MoO}_3, 3\text{P}_2\text{O}_5, 8(\text{NH}_4)_2\text{O}, \text{H}_2\text{O} + 11\text{Aq}$ , but this cannot be considered certain. A silver salt, described by Debray as belonging to this series, was examined, but the preparation was not homogeneous.

An *eighteen atom series* of sodium salts exists according to Finkener.

*Sixteen Atom Series.*—In preparing the 5·3 atom ammonium salt, a white crystalline precipitate was formed, giving on analysis—



H. B.

**Holland's Process for Melting Iridium.** By W. L. DUDLEY (*Chem. News*, 45, 168—169).—A ready method of melting iridium has been discovered by Holland, who brings a small piece of the metal to a high temperature in a hessian crucible, and then quickly adds a stick of phosphorus, when, after the fumes have cleared away, the metal is found in the molten state, having taken up a certain amount of phosphorus. Since the presence of phosphorus interferes with the use of the metal for the manufacture of the so-called "diamond pointed" pen, it is freed from this element by heating it several times to a very high temperature in a bed of lime, contained in a

hessian crucible, allowing it each time to remain in the furnace for a longer interval than during the preceding operation. According to the analyses of Clarke, a sample of the metal thus treated contains 7.5 per cent. of phosphorus. The dephosphorisation renders the metal tougher and slightly porous, but as refractory as the original.

Melted by this method, the iridium is crystalline and harder than the natural metal, being nearly as hard as the ruby; it cuts glass readily, and the hardest file is unable to touch it. It is of a steel-grey colour, is not attacked by acids, and does not tarnish. Natural grains of iridosmine are sometimes laminated in structure. Violle (this Journal, Abstr., 1880, 149) gives the melting point of iridium as  $1950^{\circ}$ .

On substituting iridium for the carbon filament in the incandescent lamp, and using it in the open air, the durability of the metal was found to be satisfactory; but a considerable increase in the amount of electricity was necessary to achieve the same result.

It has also been tried in the arc lamp, when a rod of iridium was substituted for the negative carbon of the lamp. After burning for half an hour the metal was apparently unaffected, and even after burning for 70 hours the metal suffered no appreciable loss. In this case the amount of electricity required is less than for the ordinary lamp, and the point of light is always in the same position, so that it can be used with a reflector, and the clockwork can be dispensed with. The light is very steady, since there is no burning and crumbling away of the lower point as when carbon is used.

L. T. O'S.

*Note on the preceding paper by R. B. Warder.*—The analogy between the dephosphorisation of iridium by the use of a basic lining, and that of steel is pointed out.

Fused iridium is used for the points of ruling and drawing pens, stiles and contact points for telegraphic keys, and may soon be used in the place of jewels for bearings in watches and for magnetic compass bearings.—L. T. O'S.

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### Mineralogical Chemistry.

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**Hieralite, a New Mineral.** By A. COSSA (*Compt. rend.*, **94**, 457—458).—Near the fumaroles of the crater of the island Vulcano (Lipari) are found greyish stalactiform concretions of a spongy texture, intersected by veins of selensulphur, and coated here and there with efflorescences of iron and ammonium chlorides. They contain microscopic plates of boric acid, and a large number of very small crystals. When the concretions are treated with a large quantity of water, about three-fourths dissolve, and the filtered solution, which has an acid reaction, immediately deposits a considerable quantity of gelatinous matter. This on drying is converted into a mass of small colourless monometric crystals, the principal form being the cube,

modified by the faces of the octohedron. It is potassium fluosilicate,  $K_2SiF_6$ . The author obtained 200 grams of the fluosilicate from 3 kilos. of the concretions. For this natural fluosilicate he proposes the name *hialalite*, from *Hiera*, the Greek name for the island Vulcano. Hialalite is associated in the concretions with selsulphur, realgar, mirabilite, glauberite, boric acid, and potassium, cæsium, and rubidium alums, together with compounds of arsenic, iron, thallium, zinc, tin, bismuth, lead, and copper, soluble in water. With the exception of iron, the most abundant metal in the aqueous solution is tin, possibly in the form of an alkaline fluostannate.

C. H. B.

**Spherulites in Eruptive Rocks.** By A. MICHEL-LEVY (*Compt. rend.*, **94**, 464—466).—In the optical examination of spherulites, the author has employed a parallel quartz plate, placed at an angle of  $45^\circ$  between the Nicol prisms, with the following results:—

(I.) *Felsite spherulites, with black cross (a)*, small section, very regular, and finely radiated, occurring in tertiary pearlites and rhyolites, and in permian pitchstones and felsitic porphyries. These are impregnated with colloidal opal. The fibres behave as *negative* crystals, and the spherulites owe their optical characteristics to the compression of a colloidal or vitreous substance; (*b*) spherulites of larger section from rhyolites, felsitic porphyries, and pyromerides. These are often associated with the preceding group, but the fibres are more distinct, and often show concentric zones of growth. The fibres behave as *positive* crystals, and are true quartz crystals arranged radially. Here and there, however, opal predominates.

(II.) *Felsitic spherulites with globular quartz*. These are confined to a family of acid rocks, intermediate between felsitic porphyries and the microgranulites. The fibres are entirely extinguished four times during a complete revolution of the Nicols. The spherulites are composed of a substance still partly colloidal, and when they surround a fragment of bipyramidal quartz, the extinction of the spherulite and that of the nucleus takes place at the same time.

(III.) *Felspathic spherulites*. The use of the quartz plate confirms the author's previous supposition that the spherulites of the variolite of the Durance are composed of microlites of oligoclase, which behave as *negative* crystals.

C. H. B.

**Volcanic Ash ejected from Etna on January 23, 1882.** By L. RICCIARDI (*Compt. rend.*, **94**, 586—587).—This ash has a deep grey colour, is magnetic, and when moistened has a strongly acid reaction. Water extracts from it chlorides and sulphates, and acquires an acid reaction. It is not completely decomposed by mineral acids, and when heated gives off a large quantity of sulphurous anhydride. After ignition it contains no chlorine. The ash has the following composition:—

$SiO_2$ .	$SO_3$ .	$Al_2O_3$ .	$FeO$ .	$CaO$ .	$MgO$ .	$Cl$ .	$Na_2O + K_2O$ .
37.82	20.57	9.97	14.05	11.98	3.64	1.02	0.95

It also contains traces of titanium, chromium, manganese, and phosphoric acid. Microscopic examination shows that it is composed of crystalline fragments, mixed with entire crystals of felspar, fragments

of different coloured glasses, and a large quantity of magnetite. It would appear from this that lavas exist in a crystalline condition in the interior of the volcano, and retain this condition when gradually cooled, but acquire a superficial vitreous structure if cooled rapidly.

C. H. B.

**Mineral Water from Amherst, British Burmah.** By R. ROMANIS (*Chem. News*, **45**, 158).

	$\text{CaCO}_3$ .	$\text{K}_2\text{CO}_3$ .	$\text{Na}_2\text{CO}_3$ .	$\text{MgCO}_3$ .	$\text{CaSiO}_3$ .
Parts per million..	1092·6	57·8	27·0	23·2	31·1

$\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ .  
2·8

Total.  
1244·6

L. T. O'S.

### Organic Chemistry.

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**New Compound of Carbon with Sulphur and Bromine.** By C. HELL and F. URECH (*Ber.*, 15, 273—279).—The authors at the outset draw attention to the unsatisfactory results obtained in investigations on the action of bromine on carbon bisulphide. On allowing a mixture of carbon bisulphide and bromine in the molecular proportion  $\text{CS}_2 : 2\text{Br}_2$  to stand for a day, and then subjecting the mixture to a slow distillation slightly below  $100^\circ$ , an oily residue is obtained, which does not solidify in the absence of moisture. But on the addition of water, or preferably of aqueous alcohol, colourless prismatic crystals separate out of composition  $\text{C}_2\text{S}_3\text{Br}_6$ . This compound, which the authors name *carbotrithiohexabromide*, melts at  $125^\circ$ , and decomposes at higher temperatures, with evolution of brownish-red vapours (sulphur bromide?); it is appreciably volatile at ordinary temperatures, and on slightly warming evolves a peculiar odour.

It is insoluble in water, alcohol, and ether, easily soluble in carbon bisulphide and bromine. By heating with concentrated soda or baryta solution, it is decomposed, probably thus:  $\text{C}_2\text{S}_3\text{Br}_6 + 12\text{NaOH} = 2\text{Na}_2\text{CO}_3 + \text{Na}_2\text{S}_3 + 6\text{NaBr} + 6\text{H}_2\text{O}$ ; with excess of lead oxide in presence of air, it undergoes the reaction  $\text{C}_2\text{S}_3\text{Br}_6 + 8\text{PbO} + \text{O}_2 = 2\text{PbCO}_3 + 3\text{PbBr}_2 + 2\text{PbS} + \text{PbSO}_4$ . The authors conjecture that the first product of the action of bromine on carbon bisulphide is carbodithiotetrabromide,  $\text{CS}_2\text{Br}_4$ , which they were unable to isolate in the pure state; it is probable that this compound would readily give up sulphur bromide, and yield carbotrithiohexabromide, thus:  $-2\text{CS}_2\text{Br}_4 - \text{SBr}_2 = \text{C}_2\text{S}_3\text{Br}_6$ . The authors also suggest several constitutional formulæ for this substance, but consider the formula  $\text{Br}_3\text{C.S.S.S.CBr}_3$  as the most probable.

V. H. V.

**Crystallised Anhydrous Grape-sugar.** By A. BEHR (*Chem. News*, 45, 179).—By introducing some anhydrous crystals of grape-sugar into a concentrated aqueous solution of that substance, the

author obtained large quantities of crystallised anhydrous grape-sugar, which hitherto has been obtained only from the alcoholic solution. In order to obtain the crystals readily, the solution should contain some 12 to 15 per cent. water, and should cool slowly, the temperature not falling lower than 30° C.

By keeping concentrated solutions of grape-sugar at 30° for some time, the anhydrous compound may be crystallised, without the introduction of other crystals. The crystals thus obtained dried at 30–40°, contain 0.2 per cent. moisture, estimated at 130°; they are neutral, and melt at 141–145°, and show bi-rotation. 32.68 grams of the grape-sugar, dissolved in cold water and examined immediately, gave 202–204° on the scale of a Ventzke-Soleil instrument, and on standing 24 hours 101–102°. According to Landolt it should show 100°, but this figure is calculated from an assumed specific rotation  $[\alpha]_D = 53.0$ , which is only correct for solutions containing 10 grams sugar per 100 cm. solution, but for solutions containing 32.68 grams per 100 cm.  $[\alpha]_D = 32.57$ , according to Tollens, from which 32.68 should show 101.1 on the scale, whilst actual determinations for mono-rotation gave 101–102.

Since anhydrous grape-sugar crystallises in prisms, which form loose aggregations, its crystallisation in the anhydrous state from aqueous solutions affords a ready method of separating it from the impurities formed by the action of the sulphuric acid on the sugar in its preparation from starch.

L. T. O'S.

**Specific Rotation of Maltose.** By E. SANDWIK (*Zeits. f. Physiol. Chem.*, 5, 427–430).—These investigations were made with a very pure specimen, prepared by v. Mering, and solutions of various degrees of concentration were employed. As the mean of a series of examinations, the results of which agreed very closely, the author obtained + 150 as the rotation, the same as that found by O'Sullivan. Dilution and rise of temperature did not appear to affect the rotation; on the other hand it was found to be less in freshly prepared solutions, and did not become normal for some hours.

W. N.

**Galactin.** By A. MUNTZ (*Compt. rend.*, 94, 453–455).—Powdered lucerne seeds are treated with water containing a little normal lead acetate, and the solution thus obtained is mixed with a slight excess of oxalic acid, to precipitate the lead and dissolved lime. The liquid is filtered, and the filtrate mixed with  $1\frac{1}{2}$  vols. of alcohol of 92°, when a white precipitate is obtained, which is washed with dilute alcohol, redissolved in water, and reprecipitated by addition of alcohol. When dried by exposure to air, it forms white translucent round masses, which contain small quantities of mineral matter. They swell up in water, and dissolve slowly, like gum arabic, forming a sticky but limpid solution, which is precipitated by basic but not by normal lead acetate, and behaves generally with metallic compounds like a solution of gum arabic. The substance has the composition  $C_6H_{10}O_5$ ; has a dextrorotatory power for the ray D of + 84.6°, and when treated with nitric acid yields large quantities of mucic acid. When treated with very dilute mineral acids at 100°, it is slowly converted

into a non-crystallisable sugar, and a sugar which forms hard brilliant crystals, and is identical with the  $\alpha$ -galactose obtained by Fudakowsky from milk-sugar. In consequence of this decomposition, the author proposes for the white compound the name *galactin*. This gum is widely diffused in the vegetable kingdom, and is especially abundant in the seeds of leguminous plants, particularly in those which do not contain starch. It is digested by animals, but could not be inverted by the action of saliva or pancreatic juice. It is possibly the source of the sugar in the milk of herbivora. C. H. B.

**The Mucin of *Helix Pomatia* and a New Carbohydrate (Achrooglycogen) from the same.** By H. A. LANDWEHR (*Zeitschr. f. Physiol. Chem.*, **6**, 74–78).—According to the author, when the mucin of *Helix pomatia* is treated with 1 per cent. sulphuric acid, it yields grape-sugar, whereas mucin from other sources yields only a reducing substance. The grape-sugar cannot be derived from glycogen, since the iodine reaction fails entirely in the freshly expressed secretion, and in the mucin prepared from it. The author, however, succeeded in obtaining a carbohydrate, for which he proposes the name “achrooglycogen.” In order to prepare it, he directs that the mucin obtained from the snails shall be treated with 5 to 10 per cent. caustic potash, and the proteids separated by Brücke’s solution (potassio-mercuric iodide), the solution filtered, and the filtrate precipitated by alcohol. The material thus obtained, after being washed with absolute alcohol and dried, is an amorphous, white, tasteless powder, readily soluble in water. The solution is strongly opalescent, gives no iodine reaction, and does not reduce an alkaline copper solution. By boiling with acids or by digestion with saliva or diastase, the substance is converted into dextrin and grape-sugar. W. N.

**Vasculose.** By E. FRÉMY and URBAIN (*Compt. rend.*, **94**, 108–112).—*Vasculose* may be obtained from almost any vegetable tissue, but elder-pith is preferred as yielding it in a pure state. The pith is first treated with neutral solvents and with dilute alkaline solutions, and then boiled with weak hydrochloric acid, by which the paracellulose is converted into cellulose; it is subsequently thoroughly exhausted with the ammonio-cupric reagent. The residue is vasculose, which has a slightly yellow colour, and preserves the form of the original tissue, although the latter may have lost half its substance by the removal of celluloid matters.

Vasculose is insoluble in all neutral liquids, is not changed by boiling with dilute sulphuric, hydrochloric, or phosphoric acid, or by boiling, in alkaline solutions; but it is rapidly acted on by oxidising agents, the products being a series of resinous acids, of which those first formed are almost insoluble in alcohol, whilst the last formed dissolve in that liquid and also in ether. The prolonged action of atmospheric oxygen appears also to convert vasculose into resinous acids, soluble in alkalis, and this explains the decay of certain woods on exposure to the weather. Vasculose is rapidly changed when heated *under pressure* with alkaline solutions at about 130°; by fusion with potash, it is immediately transformed into ulmic acid. This is the



source of the ulmic acid produced in the same treatment of wood, the cellulose being converted into acetic and oxalic acids. In the distillation of wood, it is more particularly the vasculose which yields the methyl alcohol and the acetic acid. The composition of vasculose is represented by the formula  $C_{36}H_{20}O_{16}$ .

Vasculose is the substance by which the cells and fibres of vegetable tissues are united, and it sometimes also forms continuous transparent membranes. The hardness of woody tissue depends on the proportion of vasculose contained in it; for instance, the wood of the poplar contains only 18 per cent. of vasculose, whilst ebony has 35 per cent., iron-wood 40 per cent., and the endocarps of nuts 60 per cent. Fibres, such as hemp and flax, are connected by layers of vasculose, the greater or less thickness of which affects the processes of retting and bleaching; and as this vasculose may be removed by suitable reagents without injury to the strength of the fibres, a certain chemical treatment according to the foregoing indications, may afterwards be found of high utility in industrial operations. R. R.

**Tertiary Amines: Influence of Heat on Allyltriethylammonium Bromide.** By E. REBOUL (*Compt. rend.*, 92, 1464—1466).—The quarternary ammonium bromides do not split up directly on dry distillation into alkyl bromide and tertiary amine bases, but give a series of other products in addition. Thus allyltriethylammonium bromide, under these circumstances, gives not only allyl bromide and triethylamine, which recombine almost wholly on cooling, but also ethylene, ethyl bromide, allyl tribromide, diethylamine, and a primary base, probably allylamine. The same products, together with ethyl allyl ether, are likewise obtained when the same bromide is distilled with potash. T. C.

**Normal Butaldehyde-ammonia and Normal Amidovaleric Acid.** By A. LIPP (*Annalen*, 211, 354—365).—When a mixture of ammonia and normal butaldehyde is exposed to a temperature of zero, rhombic pyramids of butaldehyde-ammonia, containing  $3\frac{1}{2}$  mols  $H_2O$ , are deposited. The crystals melt at  $30^\circ$ ; at a temperature above  $4^\circ$  they slowly undergo spontaneous decomposition.

The normal amidovaleric acid obtained by the addition of strong hydrochloric acid to the product of the action of hydrocyanic acid on butaldehyde-ammonia is deposited from alcohol in plates, and from an aqueous solution in needles. When cautiously heated, the crystals sublime without melting, but decompose when suddenly heated. The acid has a sweet taste.

The hydrochloride forms glistening transparent prisms, soluble in water and alcohol. The crystals deliquesce on exposure to moisture. The platinochloride,  $(C_5H_{12}NO_2Cl)_2PtCl_4$ , crystallises in yellowish-red deliquescent prisms, soluble in water and alcohol.

The nitrate forms flat needles or plates, which are sparingly soluble in alcohol, but dissolve freely in water.

The sulphate has only been obtained in the form of a syrup.

*Copper normal amidovalerate*,  $(C_5H_{10}NO_2)_2Cu$ , is a pale blue crystalline salt, sparingly soluble in water.

*Silver amidovalerate*,  $C_5H_{10}NO_2Ag$ , crystallises in microscopic prisms, sparingly soluble.

From the above description of the properties of this acid it is obvious that the amidovaleric acid discovered by Gorup-Besanez (*Annalen*, **98**, 1) is not the normal acid. W. C. W.

#### **New Combinations of Aldehydes with Phosphonium Iodide.**

By J. DE GIRARD (*Compt. rend.*, **94**, 215—217).—By the direct action of valeraldehyde on phosphonium iodide, the author has obtained a compound having the composition  $(C_5H_{10}O)_4.PH_4I$ . Propionic, salicylic, and benzoic aldehydes gave analogous compounds. R. R.

**Presence of Furfural in Fermented Liquids.** By K. FÖRSTER *Ber.*, **15**, 322—324).—In order to investigate Jorissen's reaction, and to decide the question whether the presence of fusel oil and other products is dependent on the process of fermentation, or is caused by some other change, the author has examined the distillates of fermented candy-sugar, starch-sugar, malt-liquors, and unadulterated wine. It is invariably found that these distillates contain furfural, the presence of which can be ascertained by extraction with chloroform, evaporating, taking up the residue with alcohol, and then testing with aniline and hydrochloric acid. In conclusion, the author remarks that the detection of amyl alcohol, based on Jorissen's reaction, is erroneous; that there is no satisfactory method for the quantitative estimation of small quantities of amyl alcohol in fermented liquids, and that all suspicion against the use of starch-sugar, based upon the supposed formation of a large proportion of fusel oil, must be attributed to incorrect experimental results. V. H. V.

**Nitro-acids derived from Ketones.** By G. CHANCEL (*Compt. rend.*, **94**, 399—403).—The author has continued his investigations of the acids formed by the action of nitric acid on ketones (*Compt. rend.*, **87**, 1405). *Amyl-nitrous acid*,  $C_4H_9.C(NO_2)_2H$ , obtained by the action of nitric acid on normal hexyl ketone, is a colourless oily liquid, heavier than water, and converted by reducing agents into normal valeric acid. The potassium salt forms yellow greasy-looking plates, which are only wetted with difficulty. It readily forms supersaturated solutions. The silver salt resembles the potassium compound, but is less soluble. It is not sensibly altered by exposure to light. *Butyl-nitrous acid*,  $C_3H_7.C(NO_2)_2H$ , prepared by the action of nitric acid on the more volatile portion of the crude hexyl ketone obtained from fermentation caproic acid, is a colourless oily liquid, heavier than water, and is converted into normal butyric acid by reducing agents. Its formation in this manner indicates the presence of orthovaleric acid in the caproic acid produced by fermentation. The potassium salt forms yellow prisms, and the silver salt also crystallises easily. *Hexyl-nitrous acid*,  $C_5H_{11}.C(NO_2)_2H$ , is formed, together with caproic and acetic acids, by the action of nitric acid on hexyl methyl ketone. It is a colourless oily liquid, heavier than water, and converted into normal caproic acid by reducing agents. Its formation by this reaction affords further proof of the fact that when a mixed ketone is treated with

nitric acid, the nitroxyl groups unite with the highest alcoholic radicle.

The formation of these acids is therefore characteristic of ketones containing normal alcohol-radicles. Ketones containing iso-primary radicles, however, behave differently. For example, isopentyl ketone yields *ethyl-nitrous acid* when treated with nitric acid, and isobutyl ketone behaves in a similar manner. The reaction thus distinguishes between normal and iso-primary alcohols, and may also, in certain cases, give definite indications as to the constitution of the acids and alcohols.

C. H. B.

**Action of Potassium Cyanide on Potassium Trichloracetate.** By E. BOURGOIN (*Compt. rend.*, **94**, 448—449).—In order, if possible, to obtain the compound  $C_5H_4O_8 (= C_2H_4O_2 + 3CO_2)$ , 50 grams trichloroacetic acid were dissolved in thrice their weight of water, neutralised with potassium hydrogen carbonate, and heated to about 75—85° with 100 grams powdered potassium cyanide. The products of the reaction are carbonic anhydride, hydrocyanic acid, chloroform, and potassium carbonate and chloride, together with a black substance, soluble in water, slightly soluble in alcohol, insoluble in ether. No new organic acid is formed. In this reaction the potassium cyanide acts like an alkali, thus:  $KC_2Cl_3O_2 + KHO = K_2CO_3 + CHCl_3$ . The same results are obtained when the trichloroacetic acid is only half neutralised.

When free trichloroacetic acid is treated directly with potassium cyanide at a temperature below 60°, the liquid gradually darkens, without evolution of gas, chloroform is formed, and the solution, after saturation with hydrochloric acid, yields to ether a crystalline compound, which the author is investigating.

C. H. B.

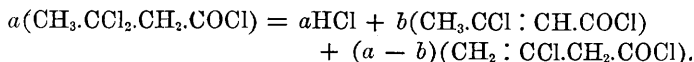
**Caproic Acid Present in Rosin Oil.** By W. KELBE and C. WARTH (*Ber.*, **15**, 308—312).—One of the authors has already shown that from the lower boiling fractions of rosin oil a number of acids of the general formula  $C_nH_{2n+1}.COOH$  can be extracted by soda, amongst which are isobutyric, caproic, and oenanthylic acids. In order to identify the caproic acid, the mixed acids were converted into ethyl salts, which were separated by fractional distillation. The ethyl caproate (b. p. 150—155°) was saponified, the potassium salt decomposed by hydrochloric acid, and the free acid distilled over. The *calcium* salt crystallises in radiating silky needles; it is less soluble in hot than in cold water; the potassium and sodium salts could not be obtained in a crystalline form. The *silver* salt separates from hot water in delicate star-like needles; the *zinc* salt forms grouped needles; the *copper* salt a dark green precipitate; the *cadmium* salt an amorphous viscous mass; and the amide, colourless needles (m. p. 95°). The acid itself is completely oxidised by alkaline permanganate solution, at least no intermediate products could be obtained. From these properties it appears that the caproic acid of rosin oil is methylpropylacetic acid,  $CHMePr.COOH$ .

V. H. V.

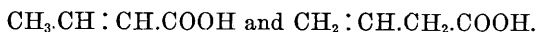
**Action of Phosphorus Pentachloride on Ethyl Acetoacetate.** By B. S. BURTON (*Amer. Chem. J.*, **3**, 27—34).—The first stage of this reaction is probably the formation of  $\beta$ -dichlorobutyric chloride,

3 b 2

according to the equation :— $\text{CH}_3.\text{CO}.\text{CH}_2.\text{COOEt} + 2\text{PCl}_5 = 2\text{POCl}_3 + \text{EtCl} + \text{CH}_3.\text{CCl}_2.\text{CH}_2.\text{COCl}$ . This compound then loses hydrogen chloride, the hydrogen being taken partly from the  $\alpha$ -position, and partly from the  $\text{CH}_3$ -group at the end, and there are formed simultaneously two isomeric chlorocrotonic chlorides, thus:—



The product treated with water gives the corresponding chlorocrotonic acids, and these are converted by sodium-amalgam into crotonic and isocrotonic acids,



The ethylic ether of methylacetoacetic acid treated in like manner might therefore be expected to yield two isomeric methylcrotonic acids, but in fact it yields only one, so that there is a very marked difference in the action of phosphorus pentachloride on the ethylic ether of acetoacetic acid, and on that of its methyl-derivative. To throw light on this difference, the author examined the action of the pentachloride on ethylic diethylacetoacetate,  $\text{CH}_3.\text{CO}.\text{C}(\text{Et})_2.\text{COOEt}$ , expecting thereby to obtain a diethylcrotonic chloride. The action, however, took place in a different way, methyl chloride being evolved, and the liquid product, when distilled in a current of steam, yielding a colourless oil, which, after treatment with caustic soda, washing with water, drying over sulphuric acid, and keeping in contact with potassium carbonate, was neutral to test-paper, and gave by analysis numbers leading to the formula  $\text{C}_7\text{H}_{11}\text{ClO}_2$ . This body is regarded by the author as probably having the constitution of a lactone,  $\text{CHCl}.\text{C}(\text{Et})_2.\text{CO}$ . When treated with sodium-amalgam, it gives up its

chlorine, and is converted into diethylacetic acid,  $\text{CH}(\text{Et})_2.\text{COOH}$ , together with another product, the nature of which has not yet been made out.

H. W.

**Ethyl Succinosuccinate, the Product of the Action of the Alkali-metals on Ethyl Succinate.** By F. HERRMANN (*Annalen*, 211, 306—343).—After referring to the investigations of Fehling (*Ann.*, 49, 192), Geuther (*Jenaische Zeitschrift für Medicin*, 2, 87), Rumpf and Remsen (*Ber.*, 8, 1409), on the action of potassium or sodium on ethyl succinate, the author describes the following method for preparing diethyl succinosuccinate. 80 grams of finely divided sodium are gradually added to 300 grams of ethyl succinate contained in a flask, which is closed by a cork provided with a mercury valve. After five or six weeks the contents of the flask are passed through a sieve to remove the unaltered sodium, the finely divided powder is treated with hydrochloric acid, and the insoluble residue is dissolved in boiling alcohol, and afterwards recrystallised from ether. Diethyl succinosuccinate forms pale green asymmetric crystals, which exhibit blue fluorescence. It is soluble in warm ether, benzene, alcohol,

petroleum spirit, carbon bisulphide, glacial acetic acid and strong sulphuric acid. At the ordinary temperature, it is but sparingly soluble in any of these menstrua. The alcoholic solution gives a cherry coloration with ferric chloride. The specific gravity of diethyl succinosuccinate at 18° is 1.4057. It melts at 156°.

By the action of potassium or sodium on a solution of diethyl succinosuccinate in benzene, or by the action of alcoholic potash or soda on the ethereal solution, one or two hydrogen-atoms are replaced by potassium or sodium, forming unstable white mono-, and red or orange coloured dimetallo-compounds.

Diethyl succinosuccinate is not acted on by acetic anhydride. It dissolves in soda-lye, forming a yellow solution, which gradually becomes colourless, and deposits some of the unaltered diethyl succinosuccinate. If carbonic anhydride is passed into the colourless alkaline liquid, the filtrate on acidification with acetic acid deposits a crystalline precipitate of monethyl succinosuccinate. The addition of hydrochloric acid to the filtrate from this precipitate throws down succinosuccinic acid.

*Monethyl succinosuccinate*,  $C_6H_5O_2.HCOOEt$ , is deposited from an ethereal solution in pale yellow prisms soluble in alcohol. It melts at 95°, with evolution of carbonic anhydride and formation of ethyl succinopropionic acid. A similar decomposition takes place on boiling this salt with water.

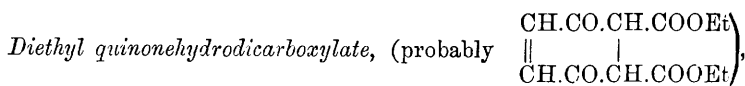
$$\begin{array}{c} CH_2.CO.CH.COOEt \\ | \\ Ethyl\ succinopropionate, \quad | \\ | \\ CH_2.CO.CH_2 \end{array}$$

is an oily liquid, soluble

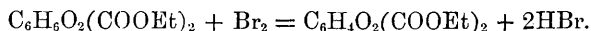
in alcohol, ether, and hot water, forming fluorescent solutions, which have a bitter taste, and give a violet coloration with ferric chloride. It cannot be distilled without decomposition, except in a current of steam.

*Succinosuccinic acid*,  $C_6H_5O_2(COOH)_2$ , forms minute needle-shaped crystals, soluble in alcohol. This solution gives a violet coloration with ferric chloride. On dry distillation, quinone tetrahydride,  $C_6H_8O_2$ , is obtained; this body unites with bromine, forming bromanil.

*Succinopropionic acid*, prepared by the action of an excess of alkali on diethyl succinosuccinate for several days, was obtained in the form of a syrup. By using a larger excess of alkali and allowing the reaction to go on for 14 days, other products are formed: the alkaline solution is neutralised with sulphuric acid, gently evaporated, and the residue extracted with alcohol. The syrup is treated with water and barium carbonate, evaporated to dryness, and again treated with alcohol, which leaves a barium salt,  $C_6H_5BaO_6 + 2H_2O$ , undissolved. The alcoholic solution deposits colourless crystals of the composition  $2(C_6H_5O_2) + H_2O$ . The crystals are soluble in water. They effloresce at 110°, and melt at 170° with decomposition. On dry distillation in a current of carbonic anhydride, quinone tetrahydride and a resinous substance are formed. The acid contained in the barium salt mentioned above crystallises in colourless rhombic plates (m. p. 139°), soluble in water and alcohol. This acid forms crystalline potassium, sodium, and ammonium salts, insoluble in alcohol. The silver salt,  $C_6H_5Ag_2O_6$ , is amorphous.



is produced by the action of bromine on a solution of diethyl succinosuccinate in carbon bisulphide,



The crude product is dissolved in dilute alkali, the solution neutralised with acetic acid, and the ethereal salt reprecipitated by carbonic acid. The pure substance is deposited from an ethereal solution in rhombic needles, and from benzene in plates. The crystals have a greenish-yellow colour, and a blue fluorescence. They melt at  $133^\circ$ , and sublime without decomposition. Diethyl quinonehydrodicarboxylate resembles diethyl succinosuccinate in its solubility in different menstrua and also in its potassium and sodium compounds.

The solution of diethyl quinonehydrodicarboxylate in soda-lye slowly changes colour. After precipitating the unaltered ethereal salt with acetic acid, barium chloride produces in the filtrate a crystalline precipitate,  $(\text{C}_{10}\text{H}_5\text{O}_6)_2\text{Ba} + 5\text{H}_2\text{O}$ , which when decomposed by hydrochloric acid yields *monethyl quinonehydrodicarboxylate*,



This acid crystallises in needles (m. p.  $184^\circ$ ) of a pale yellow colour. It is soluble in ether, alcohol, and in hot water. It forms crystalline potassium, sodium, and ammonium salts, which are easily soluble in water, yielding fluorescent solutions, from which they are reprecipitated on the addition of concentrated solutions of chlorides, nitrates, sulphates, or carbonates.

*Quinonehydrodicarboxylic acid*,  $\text{C}_8\text{H}_6\text{O}_6$ , prepared by saponifying the mono- or di-ethyl salt, is a crystalline body soluble in hot water. Ferric chloride produces a blue coloration in the aqueous solution. On rapid dry distillation it yields hydroquinol.

The following salts were prepared:  $\text{C}_6\text{H}_4\text{O}_2(\text{COOK})_2$ , straw coloured needles;  $\text{C}_6\text{H}_4\text{O}_2(\text{COONa})_2 + 2\text{H}_2\text{O}$ , pale brown efflorescent prisms. The ammonium salt, thick efflorescent prisms.  $\text{C}_8\text{H}_4\text{CaO}_6 + 5\text{H}_2\text{O}$ , pale yellow needles.  $\text{C}_8\text{H}_4\text{BaO}_6$ , flat needles, sparingly soluble in hot water.  $\text{C}_8\text{H}_4\text{Ag}_2\text{O}_6$ , insoluble yellowish-green crystalline powder. The crystalline acid potassium and sodium salts,  $\text{C}_6\text{H}_4\text{O}_2(\text{COOH}).\text{COOK}$ , and  $\text{C}_6\text{H}_4\text{O}_2(\text{COOH}).\text{COONa} + 2\text{H}_2\text{O}$ , are precipitated on addition of acetic acid to solutions of the neutral salts.

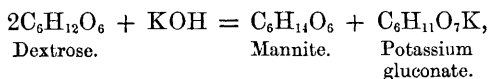
$(\text{C}_8\text{H}_5\text{O}_6)_2\text{Ca} + 5\text{H}_2\text{O}$ , pale brown needles;  $(\text{C}_8\text{H}_5\text{O}_6)_2\text{Ba}_2$ , yellowish-green needles. The neutral potassium and sodium salts give crystalline precipitates of basic salts on addition of concentrated solutions of caustic alkalis, e.g.,  $\text{C}_6\text{H}_4\text{Na}_2\text{O}_6 + 2\text{NaOH} + 10\text{H}_2\text{O}$ . Alkaline solutions of the acid reduce ammoniacal silver and copper solutions.

*Bromanil* is formed from diethyl succinosuccinate by dissolving the ethereal salt in soda-lye, neutralising with sulphuric acid after 14 days, and treating with bromine.

*Potassium nitranilate* is produced when a solution of quinonehydrodicarboxylic acid in fuming nitric acid is poured into an excess of potash.

W. C. W.

**Preparation of Lactic Acid.** By H. KILIANI (*Ber.*, 15, 136—137).—In hopes of realising the reaction represented in the equation—



the author tried the action of strong alkali on dextrose at a low temperature, and found that lactic acid was produced (compare Nencki and Sieber, this vol., 378). The process is: to 10 grams grape-sugar, dissolved in an equal quantity of water, 10 c.c. of a solution of potash (1 of KHO to  $\frac{1}{2}$  H<sub>2</sub>O) are added; the mixture is left some time at 35°, and is finally digested at 60° until the liquid ceases to reduce Fehling's solution (6—7 hours), then cold very concentrated sulphuric acid is added in quantity just sufficient to neutralise the potash used. The liquid is now evaporated down very slightly, and 93 per cent. alcohol is added until all the potassium sulphate is precipitated. The filtered alcoholic solution is boiled with zinc carbonate, and filtered; on cooling, a magma of zinc lactate separates out. In this way 27 per cent. pure lactic acid is obtained from the sugar. Soda may be used in place of potash.

D. A. L.

**Decomposition of Oxalic Acid by the Action of Aqua Regia.** By A. LONGI (*Gazzetta*, 1881, 506—512).—The author describes a number of experiments showing that oxalic acid is partially decomposed by aqua regia, though not with great facility; and therefore recommends that when this reagent is employed in the analysis of compounds or mixtures containing oxalic acid, the estimation of that acid should be made on a separate portion of the original substance.

H. W.

**Preparation of Succinic Acid from Tartaric Acid by Fermentation.** By F. KÖNIG (*Ber.*, 15, 172—173).—In a previous communication (*Abstr.*, 1881, 256) the author points out that succinic acid is the chief product of the fermentation of ammonium tartrate under the influence of putrefaction bacteria. The best yield (20 per cent.) is obtained by the following process:—To 2 kilos. of tartaric acid dissolved in water, neutralised with ammonia, and made up to 40 litres, solutions of 20 grams of potassium phosphate, 10 grams magnesium sulphate, and a few grams calcium chloride are added; this mixture is sown with 20 c.c. fermenting ammonium tartrate solution, and left at 25—30° for 6—8 weeks until all the tartaric acid is gone. The liquid is evaporated to drive off the ammonium carbonate, clarified with albumin, rendered alkaline with lime, boiled, and the calcium succinate decomposed with sulphuric acid. The succinic acid thus obtained is purified in the usual way.

D. A. L.

**Formation of Sebacic and Suberic Acids by the Distillation of Crude Fatty Acids in Superheated Steam.** By A. CAHOURES and E. DEMARÇAY (*Compt. rend.*, 94, 610—613).—The product of the distillation of crude fatty acids in superheated steam contains, in addition to paraffins and acids of the acetic series, sebacic and suberic

acids, which have probably been derived from the oleic acid present in the crude fatty acids. No other homologue of succinic acid could be detected.

C. H. B.

**Bromo-derivatives of Suberic Acid.** By F. GANTTER and C. HELL (*Ber.*, 15, 142—150).—By the action of bromine on suberic acid in presence of phosphorus, mono- or di-bromosuberic acid, or a mixture of the two, is produced, according to the quantity of bromine used. The amount of phosphorus present seems to have no influence on the reaction, for although the reaction is accelerated when a large quantity is used, the products are the same as with a small quantity. The acids can be separated from one another by the difference of their solubility in water, the monobromo-acid being easily soluble at 60—70°, whilst the dibromo-derivative is only easily soluble in boiling water. From the author's experiments, it is evident that, by the action of bromine, the suberic acid is first converted into the monobromo substituted acid, and that this by the further action of bromine is converted into the dibromo-acid. *Monobromosuberic acid* separates from its hot concentrated aqueous solution as a heavy colourless oil; this on being stirred with a glass rod, soon solidifies to a crystalline cake, which can be easily crushed to a fine powder. It separates in crystalline crusts from dilute solutions. It is insoluble in light petroleum, but soluble in alcohol and ether, and is deposited from these solutions in hard crusts, which adhere to the walls of the vessel. It melts at 102—103°: on heating more strongly it decomposes, being partially carbonised, and produces hydrobromic acid, carbonic anhydride, and suberic acid, accompanied by a characteristic aromatic odour. Boiling with alcoholic potash removes hydrobromic acid with formation of a crystalline acid (m. p. 165—170°) free from bromine, probably isomeric with xeronic acid; it is called *suberconic acid*. By the action of moist silver oxide, it yields a crystalline acid (m. p. 137°), sparingly soluble in cold water, probably either hydroxy- or ethoxy-suberic acid. By potassium cyanide, it is converted finally into suberic acid. *Dibromosuberic acid* crystallises from hot aqueous solutions in flat, white, pointed prisms (m. p. 172—173°), frequently in stellate clusters; solubilities the same as the monobromo-acid as regards other solvents than water. When it is heated slightly above its melting point, partial decomposition takes place, hydrobromic acid being evolved, and a black-brown tarry substance being formed, insoluble in water. With alcoholic potash, it gives a volatile oily acid, with a repulsive, rotten cabbage-like odour. With silver oxide, it produces an easily soluble acid, which is difficult to crystallise; it is, however, characterised by a soluble, easily crystallisable calcium salt; this acid is probably dihydroxysuberic acid.

D. A. L.

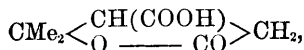
**Terebic Acid.** By W. ROSER (*Ber.*, 15, 293—297).—By the action of sodium on ethyl terebate, and subsequent treatment of the sodium compound with the haloïd ethers, the author had hoped to obtain homologues of terebic acid, but the first product of the reaction consists of the sodium salt of ethyl hydrogen teraconate, which on saponification yields teraconic acid. On substituting sodium ethylate



for the metal, sodium teraconate and succinate were obtained. As teraconic acid is closely allied to isocaproic acid, is dibasic, forms an anhydride, and with hydrobromic acid gives an acid of the  $\gamma$  series, it probably has the constitutional formula—



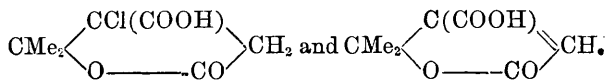
whilst terebic acid, on account of its near relation to isocapro lactone, teraconic and succinic acids, has the probable constitution—



and is homologous with paraconic and ethylidene-succinylsuccinic acid. If this view be correct, diaterebic acid is a hydroxyisopropyl succinic acid.

*Isopropylsuccinic acid*,  $\text{C}_7\text{H}_{12}\text{O}_4$ , prepared from ethyl acetate, ethyl monochloracetate, and isopropyl iodide, is a crystalline substance (m. p.  $114^\circ$ ), easily soluble in water; its calcium salt is a crystalline precipitate; it is probably identical with the acid obtained by Mielck by the action of hydriodic acid on terebic acid. By the action of phosphorus pentachloride on terebic acid, *chloroterebic acid*,  $\text{C}_7\text{O}_4\text{H}_5\text{Cl}$ , is obtained (m. p.  $191^\circ$ ; Williams, this Journal, 1874, 70). Its calcium salt forms soluble needles, and its silver salt a crystalline precipitate. On heating chloroterebic acid, hydrochloric acid is given off, and *terebilic acid* is obtained, which crystallises in rhombic tables or short prisms (m. p.  $169^\circ$ ), easily soluble in alcohol and ether; its calcium salt,  $(\text{C}_6\text{H}_7\text{O}_4)_2\text{Ca}$ , crystallises in needles; its silver salt in fine prisms.

On boiling terebilic acid with excess of potash, it gives salts analogous to the diaterebates. Chloroterebic and terebilic acids probably have the constitutional formulæ—

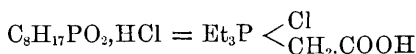


V. H. V.

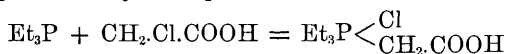
**Aconitates.** By E. GUINCHET (*Compt. rend.*, **94**, 455—457).—As a rule, the aconitates readily form supersaturated solutions, and their solutions when boiled frequently yield a precipitate, which re-dissolves more or less completely on cooling. *Monopotassium aconitate*,  $\text{C}_6\text{H}_5\text{KO}_6$ , obtained by the action of the acid on potassium carbonate, forms colourless elongated microscopic prisms, which are anhydrous, dissolve in 9 parts water at  $17^\circ$ , and begin to decompose at  $110^\circ$ . *Dipotassium aconitate*,  $\text{C}_6\text{H}_4\text{K}_2\text{O}_6 + \text{H}_2\text{O}$ , forms small, frequently naced prisms, which dissolve in 2.65 parts water at  $16^\circ$ , lose their water of crystallisation at  $130^\circ$ , and decompose at about  $150^\circ$ . *Tripotassium aconitate*,  $\text{C}_6\text{H}_3\text{K}_3\text{O}_6 + 2\text{H}_2\text{O}$ , forms slender, silky, very deliquescent needles, which lose 1 mol.  $\text{H}_2\text{O}$  at  $100^\circ$ , the other at about  $190^\circ$ , and only decompose at about  $200^\circ$ . *Trisodium aconitate*,  $\text{C}_6\text{H}_3\text{Na}_3\text{O}_6 + 2\text{H}_2\text{O}$ , retains its water in a current of air at  $50\text{--}60^\circ$ , but becomes anhydrous at  $100^\circ$ , or at ordinary temperatures in a vacuum. *Trilithium aconitate*,  $\text{C}_6\text{H}_3\text{Li}_3\text{O}_6 + 2\text{H}_2\text{O}$ , obtained by the action of the acid on lithium carbonate, forms colourless crystals, very soluble in water, giving solutions

with an alkaline reaction. It loses 1 mol.  $\text{H}_2\text{O}$  at  $145^\circ$ , and the other at  $180^\circ$ , and decomposes above  $200^\circ$ . *Dicalcium aconitate*,  $\text{C}_{12}\text{H}_8\text{Ca}_2\text{O}_{12} + 2\text{H}_2\text{O}$ , obtained by the action of the acid on lime, and allowing the solution to evaporate spontaneously, forms a gummy amorphous mass, extremely soluble in water. It loses 1 mol.  $\text{H}_2\text{O}$  at  $100^\circ$ , the second at  $130^\circ$ , and decomposes at about  $145^\circ$ . *Tricalcium aconitate*,  $\text{C}_{12}\text{H}_6\text{Ca}_3\text{O}_{12} + 3\text{H}_2\text{O}$ , obtained by the action of the acid on calcium carbonate or oxide, and evaporating the solution in the cold, forms a gummy mass, very soluble in cold water. If, however, the solution is heated to  $80$ – $90^\circ$ , or, better,  $100^\circ$ , it deposits oblique rhombic prisms, which are only slightly soluble in cold water, but if left in contact with the liquid are gradually converted into the amorphous variety and dissolve. The crystals lose 2 mols.  $\text{H}_2\text{O}$  at  $210^\circ$ , but undergo no further alteration even after prolonged heating at  $310^\circ$ . *Tristrontium aconitate*,  $\text{C}_{12}\text{H}_6\text{Sr}_3\text{O}_{12} + 3\text{H}_2\text{O}$ , closely resembles the calcium salt, dissolves in 160 parts water at  $16^\circ$ , and is precipitated on boiling the solution. It loses all its water at  $220^\circ$ , and decomposes at  $280^\circ$ . *Monobarium aconitate* forms small short colourless anhydrous prisms, which dissolve in 24 parts water at  $17^\circ$ , and decompose at  $130^\circ$ . *Tribarium aconitate*,  $\text{C}_{12}\text{H}_6\text{Ba}_3\text{O}_{12} + 3\text{H}_2\text{O}$ , is obtained as a gelatinous precipitate by adding barium chloride to aconitic acid, or a solution of an aconitate. It loses 1 mol.  $\text{H}_2\text{O}$  at  $100^\circ$ , the second at  $180^\circ$ , the third at  $200^\circ$ , and decomposes at  $280^\circ$ . *Trimagnesium aconitate*,  $\text{C}_{12}\text{H}_6\text{Mg}_3\text{O}_{12} + 3\text{H}_2\text{O}$ , obtained by the action of the boiling acid on magnesium carbonate, forms small elongated octohedrons, which dissolve in 9.6 parts water at  $17^\circ$ , and lose their water of crystallisation at  $180^\circ$ . It has an alkaline reaction. *Tricobalt aconitate*,  $\text{C}_{12}\text{H}_6\text{Co}_3\text{O}_{12} + 3\text{H}_2\text{O}$ , obtained by the action of the acid on freshly precipitated cobalt carbonate, is a rose-coloured powder, soluble in 29 parts water at  $16^\circ$ . At  $200^\circ$  it becomes deep violet, at  $215^\circ$  loses its water and acquires an intense blue colour, and decomposes at  $220^\circ$ . *Nickel aconitate* is obtained as a pale-green precipitate, containing 1 mol.  $\text{H}_2\text{O}$ , by dissolving nickel carbonate in aconitic acid and boiling; it loses its water at  $190^\circ$ , and decomposes at  $225^\circ$ . By prolonged boiling with water, it is converted into crystals of a deeper green, having the composition  $\text{C}_{12}\text{H}_6\text{Ni}_3\text{O}_{12} + 6\text{H}_2\text{O}$ . These lose their water at  $220^\circ$ , and decompose at  $230^\circ$ . *Tricadmium aconitate*,  $\text{C}_{12}\text{H}_6\text{Cd}_3\text{O}_{12} + 6\text{H}_2\text{O}$ , is obtained in the same manner in small brilliant quadratic or rhombic prisms, which dissolve in 906.5 parts water at  $17^\circ$ , become anhydrous at  $150^\circ$ , and decompose at  $180^\circ$ . *Trizinc aconitate* is obtained by dissolving the carbonate in aconitic acid. When the solution is heated in sealed tubes at  $110$ – $130^\circ$  for 70 hours, it deposits crystals of the composition  $\text{C}_{12}\text{H}_6\text{Zn}_3\text{O}_{12} + 3\text{H}_2\text{O}$ , insoluble in hot or cold water. They lose their water at  $125^\circ$ , and decompose above  $180^\circ$ . C. H. B.

**Phosphorus-betaines.** By E. A. LETTS (*Trans. Roy. Soc. Edinb.*, 1881, 30, 285–335).—These compounds, the phosphorus analogues of betaine or trimethyl-glycine,  $\text{C}_2\text{H}_2\text{Me}_3\text{NO}_2 = \text{Me}_3\text{N} < \begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix} > \text{CO}$ —or rather their haloid ethers—are formed by the action of chloracetic acid and its ethers on triethylphosphine and its homologues.

1. *Ethyllic Phosphobetaine Hydrochloride or Chlorhydrin*,

is prepared by slowly adding triethylphosphine to monochloroacetic acid and shaking the resulting solution, whereupon it separates as a dense oily layer, with great rise of temperature, rendering it necessary to keep the vessel cool, and solidifies in about an hour to a mass of colourless crystals, easily soluble in alcohol, and precipitated therefrom by cautious addition of ether to the hot solution. Its formation is represented by the equation:—



It has a sour taste and acid reaction, and is not perceptibly deliquescent. The corresponding *platinochloride*,  $(\text{C}_8\text{H}_{17}\text{PO}_2, \text{HCl})_2, \text{PtCl}_4 + \text{H}_2\text{O}$ , forms soluble light orange-coloured crystals, which sometimes attain a large size.

The *hydroxide*,  $\text{Et}_3\text{P}(\text{OH}).\text{CH}_2.\text{COOH}$ , prepared by decomposing the hydrochloride in aqueous solution with silver oxide, and evaporating the solution in a vacuum, is crystalline and extremely deliquescent. When exposed for some months in a vacuum over sulphuric acid, it gives off 1 mol. water, and is converted into the anhydrous base:  $\text{Et}_3\text{P}(\text{OH}).\text{CH}_2.\text{COOH} = \text{H}_2\text{O} + \text{Et}_3\text{P} < \begin{smallmatrix} \text{CH}_2 \\ -\text{O} \end{smallmatrix} > \text{CO}$ .

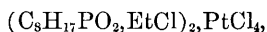
This decomposition is analogous to that of hydrated dimethylthetine,  $\text{Me}_2\text{S}(\text{OH}).\text{CH}_2.\text{COOH}$ , which, by abstraction of  $\text{H}_2\text{O}$ , is converted into  $\text{Me}_2\text{S} < \begin{smallmatrix} \text{CH}_2 \\ -\text{O} \end{smallmatrix} > \text{CO}$ .

The *hydrobromide* or *bromhydrin* of phosphobetaine,



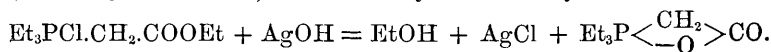
prepared by treating the solution of the hydroxide with hydrobromic acid, forms colourless very thin quadratic plates, somewhat deliquescent, but in other respects resembling the hydrochloride. The *hydroiodide*,  $\text{Et}_3\text{PI}.\text{CH}_2.\text{COOH}$ , prepared in like manner, forms small granular crystals. The *sulphate*,  $(\text{Et}_3\text{P}.\text{CH}_2.\text{COOH})_2\text{SO}_4$ , prepared by decomposing the hydrochloride with silver sulphate and evaporating in a vacuum, forms a solid crystalline mass.

*Ethyllic Phosphobetaine Ethochloride* or *Chlorethylin*,  $\text{C}_{10}\text{H}_{22}\text{ClPO}_2 = \text{C}_8\text{H}_{17}\text{PO}_2, \text{EtCl} = \text{Et}_3\text{P}.\text{Cl}.\text{CH}_2.\text{COOEt}$ , is obtained by the action of ethyl chloracetate on triethylphosphine, as a colourless syrup, solidifying after a few minutes to a crystalline mass. It is extremely deliquescent, and cannot be recrystallised. Its *platinochloride*,

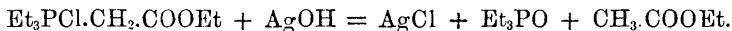


crystallises in light orange-coloured plates.

*Action of Silver Oxide on the Chlorethylin*.—According to Hofmann (*Proc. Roy. Soc.*, **11**, 550), this reaction yields the anhydrous base: thus—



Letts confirms this statement, but finds in addition that, when the two bodies are mixed in aqueous solution, a strong smell of ethyl acetate is evolved, whence he infers that a second reaction probably occurs at the same time, resulting in the formation of triethylphosphine oxide and ethyl acetate, thus:—



The *bromethylin* and *iodethylin* of ethylic phosphobetaine resemble the *chlorethylin* in their properties and reactions, and are obtained in like manner by the action of ethylic bromacetate and iodacetate on triethylphosphine, the action however in both cases being more energetic than that of the chlorine-compound. This is remarkable, inasmuch as bromacetic acid itself does not, except under special conditions, react with triethylphosphine in such a manner as to form a phosphobetaine.

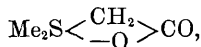
*Action of Heat on Ethylic Phosphobetaine Compounds.*—The bromethylin, when heated, gives off gas consisting in great measure of carbonic anhydride, and yields a solid product which, when crystallised from chloroform, has the composition of triethylmethylphosphonium bromide,  $\text{Et}_3\text{MePBr}$ . The corresponding *platinochloride*,



crystallises in orange-coloured octohedrons with truncated summits. The *chlorethylin* decomposes in like manner, yielding  $\text{Et}_3\text{MePCl}$  and a mixture of carbonic anhydride and ethylene:  $\text{Et}_3\text{PCl} \cdot \text{CH}_2 \cdot \text{COOEt} = \text{Et}_3\text{MePCl} + \text{CO}_2 + \text{C}_2\text{H}_4$ . The chlorhydrin also decomposes in a similar manner, but the action is much more definite, and the gas evolved is pure carbonic anhydride:  $\text{Et}_3\text{PCl} \cdot \text{CH}_2 \cdot \text{COOH} = \text{Et}_3\text{MePCl} + \text{CO}_2$ . The *sulphate* decomposes in an exactly similar manner.

The free base (hydroxide), when its aqueous solution is concentrated by boiling, gives off a faint odour of triethylphosphine, and the concentrated solution evaporated in a vacuum, leaves a solid mass which effervesces with acids, has a faint acid reaction, and in fact behaves like an acid carbonate. It is in fact the acid carbonate of triethyl-methyl-phosphonium, a compound isomeric with the base itself:— $\text{Et}_3\text{P}(\text{OH}) \cdot \text{CH}_2 \cdot \text{COOH} = \text{Et}_3\text{PMe} \cdot \text{O} \cdot \text{COOH}$ .

These decompositions of ethylic phosphobetaine compounds are similar of those of the oxy-salts of dimethyl-thetine,



and afford another of the many instances in which analogous compounds of sulphur and phosphorus exhibit similar properties, whilst the corresponding compounds of nitrogen behave differently; betaine salts, for example,  $\text{Me}_3\text{N}(\text{R}) \cdot \text{CH}_2 \cdot \text{COOH}$  [R denoting Cl, Br, &c.] being resolved by heat into trimethylamine and a derivative of acetic acid, or simply volatilising without change.

*Action of Potassium Hydroxide on Ethylic Betaine-compounds.*—The chlorhydrin is decomposed by potash, with formation of triethylphosphine oxide,  $\text{Et}_3\text{PCl} \cdot \text{CH}_2 \cdot \text{COOH} + 2\text{KOH} = \text{Et}_3\text{PO} + \text{KCl} + \text{CH}_3 \cdot \text{COOK} + \text{H}_2\text{O}$ . The hydroxide is decomposed in the same

manner:  $\text{Et}_3\text{P}(\text{OH})\cdot\text{CH}_2\cdot\text{COOH} + \text{KOH} = \text{Et}_3\text{PO} + \text{CH}_3\cdot\text{COOK} + \text{H}_2\text{O}$ . With the chlorethylin, the products are triethylphosphine oxide, potassium chloride, and ethyl acetate:  $\text{Et}_3\text{PCl}\cdot\text{CH}_2\cdot\text{COOEt} + \text{KOH} = \text{Et}_3\text{PO} + \text{KCl} + \text{CH}_3\cdot\text{COOEt}$ . The action of oxidising and reducing agents on the chlorhydrin did not yield any definite products.

*Action of Bromacetic Acid on Triethylphosphine.*—This action is very different from that which takes place with chloracetic acid. It varies with the temperature, and the nature of the products has not yet been distinctly made out; but the author thinks he has proved that at low temperatures the two bodies react so as to produce about equal quantities of triethylphosphobetaine hydrobromide and triethylphosphine acetobromide, or a mixture of the latter with triethylphosphine bromacetate. At intermediate temperatures, very little of the hydrobromide is formed, and the product consists of the bromacetate and acetobromide, whilst at higher temperatures the acetobromide is almost the only product.

H. W.

**Formation of Urea from Ammonia and Carbon Dioxide.** By W. G. MIXTER (*Amer. Chem. J.*, **4**, 35—38).—These gases do not act on one another at a heat below visible redness; but when they are passed together through a red-hot tube, products are formed, which yield urea beautifully crystallised in the cooler parts of the tube, where the heat is nevertheless sufficient to prevent the condensation of ammonium carbamate and carbonate. The urea cannot, however, be the direct product of the reaction, inasmuch as it is decomposed at the temperature of the experiment. Its formation is doubtless preceded by that of other bodies, and probably by that of cyanic acid, according to the equation  $\text{CO}_2 + \text{NH}_3 = \text{H}_2\text{O} + \text{CNOH}$ , the cyanic acid then uniting with ammonia in the cooler part of the tube to form urea. The production of urea by passing a mixture of air, ammonia, and benzene over a hot coil of platinum, observed by Herroun (this Journal, 1881, Trans., 471), was probably due to the action of ammonia on carbon dioxide resulting from the action of air on benzene. That the formation of urea in the manner above described is preceded by that of cyanic acid, is corroborated by the fact that a cyanate is formed when dry carbon dioxide and pure dry ammonia are passed through a red-hot tube containing carbonate of potassium or sodium.

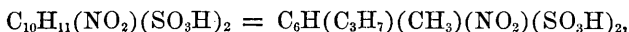
The production of cyanates from alkali carbonates, ammonia and carbon dioxide, is not accompanied by that of cyanides when pure ammonia is used; but when commercial ammonia-water of good quality was employed, the solution of the saline mass gave a distinct reaction of cyanides with ferroso-ferric sulphate and an acid.

H. W.

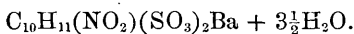
**Benzene, Dipropargyl, and Acetylene: Constitution of Benzene.** By J. THOMSEN (*Ber.*, **15**, 328—331).—The author has re-determined the heats of combustion of benzene and acetylene, and also determined that of dipropargyl. From the present researches the heat of combustion of acetylene at  $19^\circ$  is 310,340 cal. per molecule (former value 310,570 cal.); the mean value can be taken as 310,450

calcs. As it appears that the benzene used in the former experiments was probably contaminated with foreign bodies, adhering to the crystals separated out by freezing, the author prepared benzene by the distillation of calcium benzoate (from natural hippuric acid) with soda lime. The heat of combustion of the purified benzene at  $19^{\circ}$  was found to be 787,950 calcs. per molecule, a value about 2 per cent. lower than that obtained in former experiments (Abstr., 1881, 89), this difference being due partly to a mistake in the former calculations, and partly to the impurities of the benzene. The heat of combustion of dipropargyl at  $19^{\circ}$  was found to be 883,230 calcs. per molecule. So the difference between the heats of combustion of dipropargyl and benzene is  $883,230 - 787,950 = 95,280$ , this being due to a difference of constitution of the two substances. Dipropargyl contains three single and two triple bonds, whilst benzene, according to the author, contains nine single bonds. If  $V$  and  $V_3$  represent the heat energy of the single and triple bonds respectively, then the difference between the heats of combustion of the two compounds is equal to the differences between the heat energy of the triple or single bonds contained in them, or  $6V_1 - 2V_3 = 952,010$  calcs., or  $3V_1 - V_3 = 47,640$  calcs. Similarly, the difference between the heats of combustion of 3 mols. of acetylene (containing altogether three triple bonds) and 1 mol. of benzene is  $931,380 - 787,980 = 143,400 = 9V_1 - 3V_3$  or  $47,800 = 3V_1 - V_3$ , a value approximately equal to that deduced from a comparison of the heats of combustion of benzene and dipropargyl. This concordance is a further strong argument for the hypothesis that the six atoms of benzene are combined together by nine single and not by three single and double bonds (cf. *suprà*). V. H. V.

**Action of Sulphuric Chlorhydrin on Nitrocymene.** By T. LEONE (*Gazzetta*, 1881, 512—514).—The product of this reaction is a *nitrocymenedisulphonic acid*,



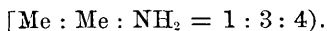
the *barium salt* of which crystallises in very slender white needles, extremely soluble in water, very slightly in ordinary, quite insoluble in absolute alcohol, and having the composition—



The *lead salt* crystallises in needles containing  $4\frac{1}{2}\text{H}_2\text{O}$ , very similar to the barium salt, but not so well defined. The free acid has not been obtained in crystals. H. W.

**Synthesis of Homologues of Aniline from Bromaniline.** By A. CLAUS (*Ber.*, 15, 315—319).—The formation of azobenzene by the action of sodium on bromaniline has been explained by Anschütz and Schultz (Abstr., 1878, 49) on the supposition of the oxidation of an intermediate compound,  $\text{C}_6\text{H}_5\text{NHNa}$ . On the other hand, the author considers that the bromine is removed by the sodium, and the residue  $\text{C}_6\text{H}_4\text{NH}_2$  is decomposed thus:  $4(\text{C}_6\text{H}_4\text{NH}_2) = \text{PhN:NPh} + 2\text{PhNH}_2$ . If this view were correct, then the action of sodium in the

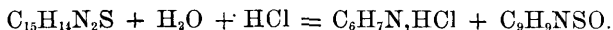
presence of an alcoholic bromide should yield a homologue of aniline. This is confirmed by experiment, parabromotoluidine and methyl iodide with sodium yielding xylidine, of probable constitution



A corresponding reaction of sodium on normal propyl bromide and parabromaniline yielded unsatisfactory results. V. H. V.

**Oxypropyltoluidine.** By R. F. MORLEY (*Ber.*, 15, 179—180).—By heating a mixture of [1 : 4] toluidine and propylene oxide on a water-bath for four hours, *oxypropyltoluidine*,  $\text{C}_3\text{H}_7\text{O.NH.C}_6\text{H}_7$ , is formed. It is crystalline (m. p.  $74^\circ$ ; b. p. about  $290^\circ$ , with partial decomposition); becomes slightly coloured from exposure to air, is insoluble in water, but easily soluble in benzene and ether. Gold chloride precipitates an oily salt from the aqueous solution of its hydrochloride. D. A. L.

**Compounds formed by the Action of Alcoholic Iodides on Thiocarbanilide.** By W. WILL (*Ber.*, 15, 338—348).—A continuation of the author's researches (Abstr., 1881, 905). Ethyl phenylimido-phenylthiocarbamate is decomposed on dry distillation into mercaptan and carbanilide, thus:  $\text{NPh} : \text{C}(\text{SEt}).\text{NPh} = \text{C}(\text{NPh})_2 + \text{EtSH}$ . The alkyl salts of phenylimidophenylcarbamie acid, heated with dilute sulphuric acid at  $160$ — $180^\circ$  in sealed tubes, are decomposed with formation of aniline and an alkyl salt of phenylcarbamioethioic acid, thus:  $\text{NPh} : \text{C}(\text{SMe}).\text{NPh} + \text{H}_2\text{O} = \text{SMe.CO} : \text{NPh} + \text{PhNH}_2$ . The latter gives a golden-coloured precipitate with thallous oxide, and with lead and silver nitrate a white precipitate. On heating the methyl salt of phenylimidophenylcarbamie acid with carbon bisulphide, phenylthiocarbimide and the methyl salt of phenyldithiocarbamic acid are formed thus:  $\text{NPh} : \text{C}(\text{MeS}).\text{NPh} + \text{CS}_2 = \text{CSNPh} + \text{SMe.CS.NPhH}$ . By the action of ethylene bromide on thiocarbanilide, an ethylene phenylimidophenylthiocarbamate is obtained, which boils with slight decomposition at  $300^\circ$ ; it combines with most acids to form well crystallised salts; it is not altered by boiling with dilute hydrochloric or sulphuric acid, but on heating it at  $200^\circ$  with these acids, the ethylene salt of phenylcarbamioethioic acid is obtained, thus:

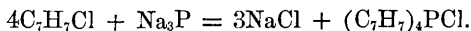


The latter substance crystallises in colourless needles (m. p.  $79^\circ$ ), easily soluble in alcohol and ether; its solutions are not precipitated by thallous oxide.

With carbon bisulphide, ethylene phenylimidophenylcarbamate yields phenylthiocarbimide and the ethylene salt of phenyldithiocarbamic acid, thus:  $\text{NPh} : \text{C} < \begin{smallmatrix} \text{NPh} \\ \text{S.CH}_2 \end{smallmatrix} > \text{CH}_2 + \text{CS}_2 = \text{SC} < \begin{smallmatrix} \text{NPh} \\ \text{S.CH}_2 \end{smallmatrix} > \text{CH}_2 + \text{CSNPh}$ . This compound forms pointed crystals (m. p.  $134^\circ$ ), insoluble in cold water, dilute acids and alkalis; it is not easily attacked by oxidising agents; it combines directly with methyl iodide to form a crystalline substance of the composition  $\text{C}_9\text{H}_9\text{NS}_2.\text{IMe}$ , to which the author

assigns the probable constitution  $\text{MeS.Cl} < \begin{smallmatrix} \text{NPh} \\ \text{S.CH}_2 \end{smallmatrix} > \text{CH}_2$ . In conclusion, the author remarks that the ready solubility of thiocarbamide in alkalis, taken in connection with the formation from it, by its combination with halogen derivatives of hydrocarbons, of bases which yield mercaptans on decomposition, points to the constitutional formula  $\text{NH} : \text{C}(\text{SH}).\text{NH}_2$ . The author is engaged in similar experiments on the corresponding toluidine derivatives. V. H. V.

**Tetrabenzylphosphonium Salts.** By E. A. LETTS and N. COLLIE (*Trans. Roy. Soc. Edinb.*, **30**, 181—215).—The chloride is obtained by the action of benzyl chloride on sodium phosphide (prepared by adding phosphorus in small pieces to a solution of sodium in xylene):



The quantity obtained varies however considerably according to the manner in which the phosphide of sodium is prepared, and the proportions of phosphorus, sodium, benzyl chloride, and xylene employed (for details see the original paper). The tetrabenzylphosphonium chloride is dissolved out of the product by boiling water, and on cooling crystallises in splendid needles, sometimes  $1\frac{1}{2}$  inches long, and containing water of crystallisation which is given off on heating. The dried salt melts at about  $224$ — $225^\circ$ , and at higher temperatures undergoes a complex decomposition, yielding toluene, stilbene, and apparently dibenzyl, together with a considerable quantity of charred residue. The *platinochloride*,  $2(\text{C}_7\text{H}_7)_4\text{PCl.PtCl}_4$ , is very slightly soluble in water and in alcohol, and separates from the alcoholic solution in light orange-coloured leaflets. The *acid sulphate*,  $(\text{C}_7\text{H}_7)_4\text{PHSO}_4$ , formed by treating a solution of the chloride with silver sulphate, or by warming the dry chloride with strong sulphuric acid, is more soluble than the chloride, and separates in plates from a hot and somewhat concentrated aqueous solution. The *normal sulphate* has not yet been obtained. The *hydroxide* is formed by the action of barium hydroxide or carbonate on the acid sulphate, and separates from the filtrate after boiling, concentration, and remaining at rest for a couple of days, in large highly refractive rhombohedral plates, very soluble even in cold water, also in alcohol, from which it separates in crystals containing alcohol of crystallisation. Its solutions have an alkaline reaction, and neutralise acids, yielding salts of tetrabenzylphosphonium. The anhydrous base begins to melt at  $190^\circ$ , but a portion remains unfused up to  $211^\circ$ , so that it seems to be incapable of melting without decomposition. At higher temperatures it decomposes, yielding liquid and solid products.

In attempting to prepare the hydroxide with solutions of baryta and tetrabenzylphosphonium sulphate more concentrated than those above mentioned, the filtered solution did not yield any base, but the precipitated barium sulphate was found to contain a substance insoluble in water but soluble in alcohol, and separating therefrom in white needles, melting at  $210$ — $212^\circ$ , and consisting of tribenzylphosphonium oxide, formed together with toluene by decomposition of the hydroxide,  $(\text{C}_7\text{H}_7)_4\text{POH} = \text{C}_7\text{H}_8 + (\text{C}_7\text{H}_7)_3\text{PO}$ , this decomposition



being exactly analogous to that of tetrethylphosphonium hydroxide into triethylphosphine oxide and ethane.

Various salts of tetrabenzylphosphonium may be obtained by treating the acid sulphate with the corresponding barium salts. The *bromide* crystallises in long silky needles, less soluble in water than the chloride, melting at  $216\text{--}217^\circ$ . The *iodide* is almost insoluble in water, but soluble in aqueous alcohol, and crystallises therefrom in needles resembling the chloride. The *chlorate* crystallises from a moderately strong solution in long needles, and puffs when heated above its melting point. The *chromate*, prepared by the action of silver chromate on a solution of the chloride, crystallises in small lemon-yellow plates on exhausting the precipitate with boiling alcohol, and adding water to the filtered solution. The *nitrate*, obtained by saturating the base with nitric acid, crystallises in long silky needles. The *acetate*, obtained by the action of the chloride on silver acetate, is the most soluble of all the known salts of tetrabenzylphosphonium, and crystallises from alcohol with difficulty. The *oxalate*, obtained by saturation, crystallises in long needles.

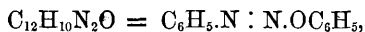
*Examination of the Residues from the Preparation of Tetrabenzylphosphonium Chloride.*—When the product of the action of benzyl chloride on sodium phosphide is repeatedly boiled with water to extract the tetrabenzylphosphonium chloride, there remains an orange-coloured mass, which may be split up into three portions: (1) soluble in chloroform only; (2) soluble in chloroform and alcohol; (3) soluble in chloroform, alcohol, and a mixture of alcohol and water. This last portion, freed from colouring matter by digestion with ether or carbon sulphide, and further purified by one or two crystallisations from hot alcohol, forms shining strongly refractive needles, melting at  $212^\circ\text{C}$ ., apparently volatilising unchanged, and having the composition of tribenzylphosphine oxide,  $(\text{C}_7\text{H}_7)_3\text{PO}$ . The same compound was obtained in opaque plates by the action of caustic baryta on the acid sulphate of tetrabenzylphosphonium, and in very bulky silky needles by the action of sodium on tetrabenzylphosphonium chloride, the oxygen being probably due to access of air. All these varieties yield the same platinumchloride,  $4(\text{C}_7\text{H}_7)_3\text{PO}, 2\text{HCl}, \text{PtCl}_4$ , in the form of a light orange-coloured powder, made up of cruciform or radiate groups of microscopic needles. The oxide, when heated, partly volatilises unchanged, and is partly resolved into toluene, free phosphorus, charred matters, and very small quantities of other substances. A *brominated compound*,  $5(\text{C}_7\text{H}_7)_3\text{PO}, 4\text{Br}_2$ , is obtained by adding bromine in excess to a solution of tribenzylphosphine oxide in glacial acetic acid at the boiling heat, and separates on cooling in the form of a bright yellow crystalline powder. A *sulphuretted compound*,  $5(\text{C}_7\text{H}_7)_3\text{PO}, \text{S}$ , is formed when the oxide is melted with sulphur in the proportion  $(\text{C}_7\text{H}_7)_3\text{PO} : \text{S}_2$  at  $240^\circ$ , or rather higher. The product dissolves completely in a large quantity of boiling alcohol, and separates on cooling in light buff-coloured silky needles; it is insoluble in water, slightly soluble in alcohol, and melts at  $211\text{--}212^\circ$ .

*Examination of the Residue Soluble in Chloroform and Alcohol only.*—This portion of the residue was contained in the dark-brown mother-liquors of the tribenzylphosphine oxide, and remained, on evaporating off the alcohol, as a dark-brown syrupy mass, which on cooling solidified

to a resin; and this, when heated, split up into free phosphorus, stilbene, dibenzyl, and toluene, a result which may be explained on the supposition that the resin consisted mainly of tribenzylphosphine,  $2(\text{C}_7\text{H}_7)_3\text{P} = \text{P}_2 + \text{C}_{14}\text{H}_{12} + \text{C}_{14}\text{H}_{14} + 2\text{C}_7\text{H}_8$ . Attempts to prepare tribenzylphosphine by the action of metallic sodium and of sodium phosphide on tetrabenzylphosphonium chloride did not yield definite results.

H. W.

**Oxyazobenzene and some of its Derivatives.** By S. SCICHLONE (*Gazzetta*, 1882, 108—112).—*Oxyazobenzene*,



was discovered in 1866, by Griess, who obtained it by the action of barium carbonate on diazobenzene nitrate; Kekulé and Hidegh afterwards prepared it by the action of diazobenzene nitrate on potassium phenate; Mazzara obtained it by mixing dilute solutions of aniline nitrate, potassium nitrite, and phenol; and lastly, Wallach and Kiepenheuer prepared it by heating azoxybenzene,  $(\text{C}_6\text{H}_5\text{N})_2\text{O}$ , with sulphuric acid.

Griess obtained, together with the oxyazobenzene, a substance melting at  $131^\circ$ , and having the composition of *bidiazobenzenephenol*,  $\text{C}_{18}\text{H}_{14}\text{N}_4\text{O} = \text{C}_6\text{H}_4(\text{C}_6\text{H}_5\text{N}_2)_2\text{O}$ . Scichilone, following Mazzara's process, obtained a product separable by fractional crystallisation into three portions, the first consisting of oxyazobenzene in violet-red crystals melting at  $154^\circ$ ; the second of orange-yellow colour, and melting at  $142$ — $149^\circ$ ; the third melting at  $130$ — $132^\circ$ . The second and third portions were not homogeneous, but mixtures of very brilliant yellow needles with reddish-yellow laminae having a violet reflex. A fourth portion, obtained from the mother-liquors after standing for 24 hours, consisted of yellow needles melting at  $96^\circ$ . The laminae were merely a new modification of oxyazobenzene; the yellow needles gave by analysis 73.95 per cent. carbon and 6.08 hydrogen, agreeing approximately with the formula of *bidiazobenzenephenol*, which requires 71.25 C. and 4.97 H.

*Acetyl-oxyazobenzene*,  $\text{C}_6\text{H}_5\text{.N:N.OC}_6\text{H}_4\text{Ac}$ , obtained by heating oxyazobenzene with acetic anhydride, crystallises from boiling alcohol in very beautiful orange-yellow scales melting at  $84.5^\circ$ .—*Methyloxyazobenzene*,  $\text{C}_6\text{H}_5\text{.N:N.OC}_6\text{H}_4\text{Me}$ , is prepared by cohobating for three-quarters of an hour, oxyazobenzene (10 g.) with methyl iodide (7.5 g.) and potassium hydroxide (3 g.) dissolved in a small quantity of methyl alcohol, and separates, on pouring the cooled mass into water, in the form of a heavy oil, which soon solidifies, and may be obtained by crystallisation from alcohol in fine large brownish-yellow needles melting at  $53.5$ — $54^\circ$ .

*Bromine* acts directly on oxyazobenzene dissolved in acetic acid, forming a substance which crystallises in dark-yellow needles melting at  $139.5^\circ$ .

*Action of Reducing Agents.*—Neither oxyazobenzene nor its acetyl-derivative appears to be acted upon by zinc; but when an alcoholic solution of oxyazobenzene is treated with sodium-amalgam, dark-

yellow laminæ are formed, melting at  $90^{\circ}$ ; but the quantity obtained was too small for examination.

*Action of  $\text{CO}_2$  and Sodium.*—This action, which begins at  $160^{\circ}$ , and is very energetic, was expected to yield an acid isomeric with that which Griess lately obtained by the action of diazobenzoic acid on phenol, but the result was negative. H. W.

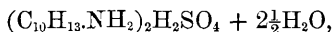
**Synthesis of Homologous Phenols.** By A. LIEBMANN (*Ber.*, 15, 150—154).—The author now gives some additional details, &c., to his former paper (this vol., 171). In the preparation of isobutyl and amyl phenols, it is advantageous to heat the mixture of phenol, alcohol, and zinc chloride strongly until  $180^{\circ}$  is reached, and then to keep it at this temperature as long as the operation lasts (about 45 minutes). *Isobutylphenolsulphonic acid* is obtained when the phenol is warmed with fuming sulphuric acid; *barium isobutylphenolsulphonate* forms warty crystalline lumps, which crumble in the desiccator. Amyl and benzyl phenols are best purified by treating the product of the reaction, first with soda, then with steam, and finally with hydrochloric acid, the mixture of phenol and amyl- or benzylphenol thus obtained being fractionally distilled. Benzylphenol boils in a current of carbonic anhydride at  $325\text{--}330^{\circ}$ , and melts at  $84^{\circ}$ . It is identical with the body obtained by Paternò (*ibid.*, 5, 288, and 435) by the action of benzyl chloride on phenol in presence of zinc-dust. The author suggests that this reaction is not due to the metallic zinc, but to the zinc chloride formed by the action of the free hydrochloric acid in the benzyl chloride on the zinc. In one experiment, a mixture of 1 mol. phenol and 1 mol. benzyl chloride with a trace of zinc chloride, gave off a stream of hydrochloric acid, became very hot, and yielded as chief products benzylphenols (m. p.  $84^{\circ}$ ), hence supporting the suggestion. Amylphenol could not be obtained in this way.

By the action of 2 mols. alcohol on 1 mol. salicylic acid in presence of zinc chloride, a body (probably ethylsalicylic acid) is formed, which decomposes on distillation into butylphenol and carbonic anhydride.

D. A. L.

**Synthesis of Thymol from Cumaldehyde.** By O. WIDMANN (*Ber.*, 15, 166—172).—The author has already (*Abstr.*, 635, 1880) described a method by which metatoluidine can be prepared from benzaldehyde. The benzaldehyde was nitrated, the nitro-body was converted by phosphorus pentachloride into metanitrobenzal chloride, and this, by reduction with zinc and hydrochloric acid, at first at a low temperature, and finally by boiling, yielded metatoluidine. He has now succeeded in preparing thymol from cumaldehyde, synthetically, by a similar series of reactions, making it probable that this reaction is a general one for the conversion of aldehyde-groups into methyl-groups. The *cumaldehyde* (b. p.  $236^{\circ}$ ), purified by means of the sodium sulphite compound, is converted into *nitrocumaldehyde* (m. p.  $54^{\circ}$ ), purified by crystallisation from alcohol, and treated with phosphorus pentachloride (8 grams to 7 of nitrocuminol), avoiding too great a rise of temperature. On pouring the product into water, *nitrocymylene chloride*,  $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Pr}\cdot\text{CHCl}_2$ , separates as an oil solidifying at  $-10\text{--}20^{\circ}$ , heavier than water, soluble

in alcohol and ether. To convert this nitro-compound into the amido-derivative the alcoholic solution is mixed with strong hydrochloric acid, cooled, and treated with zinc in small quantities, not allowing the temperature to rise above  $12^{\circ}$ . The alcohol is then evaporated, the residue neutralised with soda, sodium acetate added, and the *cymidine*,  $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{PrMe}$ , thus precipitated, is distilled with steam. It is a colourless oil, lighter than water, and of repulsive odour. It is only slightly soluble in water, but easily in alcohol and ether. It shows no reactions either with litmus or with sodium hypochlorite, or with potassium chromate and sulphuric acid, &c., but fumes strongly with hydrochloric acid. It is stable in air, and colours a deal shaving yellow. Cymidine hydrochloride,  $\text{C}_{10}\text{H}_3\cdot\text{NH}_2\cdot\text{HCl}$ , is an oil which solidifies to a white mass of fine silky needles. Cymidine sulphate,



crystallises in white needles, easily soluble in warm, sparingly soluble in cold water. *Cymidine platinochloride*,  $(\text{C}_{10}\text{H}_{13}\cdot\text{NH}_2\cdot\text{HCl})_2\cdot\text{PtCl}_4$ , forms pale yellow brilliant needles, sparingly soluble in water, more easily in alcohol and ether. Cymidine acetate crystallises in white needles (m. p.  $112^{\circ}$ ). These properties agree passably with those of Barlow's cymidine (*Annalen*, **98**, 245). It may be converted into thymol in the following manner: cymidine sulphate is dissolved in water and mixed with less than 1 mol. potassium nitrite in the cold, and then acidified with dilute sulphuric acid, and the product distilled with steam, when the *thymol* passes over. It crystallises in rhombic prisms (m. p.  $44^{\circ}$ ), and shows all the reactions for ordinary thymol. *Nitrosothymol* remains behind in the flask after the distillation, crystallises out on cooling as a bulky jelly of yellowish-white fine needles (m. p.  $160$ — $162^{\circ}$ ), nearly insoluble in cold, and only sparingly in boiling water; it, however, dissolves easily in alkalis and alkaline carbonates; some pure nitrosothymol from natural thymol was prepared and compared with this, and the two were found to be identical.

This reaction supports the view that, when an aromatic aldehyde containing the aldehyde-group in the benzene-ring is nitrated, the nitro-group goes in the meta-position to the aldehyde-group; and further, it forms a basis for the assumption that the hydroxyl in thymol occupies the meta-position to the methyl. D. A. L.

**New Isomeride of Orcinol.** By E. KNECHT (*Ber.*, **15**, 298—302).—The author draws attention to the fact that orcinol, although containing the two hydroxyl-groups in relatively the same position as resorcinol, and therefore a true homologue of it, yet differs from it in giving no fluorescein reaction. He has accordingly isolated another dihydroxytoluene, which, as shown from its method of preparation, likewise contains the two hydroxyl-groups in the meta-position.

From dinitrotoluene a *mononitrocresol* was obtained, which forms golden needles (m. p.  $78^{\circ}$ ), sparingly soluble in cold water, easily soluble in hot water, alcohol, and benzene; its methyl ether is a golden-yellow oil (b. p.  $267^{\circ}$ ), volatile in a current of steam. The mononitrocresol was reduced by tin and hydrochloric acid to amidocresol, the

hydrochloride of which was converted by the diazo reaction into *dihydroxytoluene*, which the author proposes to name *cresorcinol*. This substance forms white monosymmetrical crystals (m. p.  $103^{\circ}$ ), easily soluble in water, alcohol, and ether; it resembles resorcinol in its reactions with lead acetate, silver nitrate, bromine-water, and phthalic anhydride. With the latter, it forms a fluorescein, which gives a fluorescent solution with alkalis. This dihydroxytoluene differs, however, from resorcinol in its crystalline form, those of the former being monosymmetrical, those of the latter rhombic. With ferric chloride, the dihydroxytoluene gives an evanescent green coloration.

The author draws attention to the easy conversion of the metamido phenols and amidocresols into the corresponding dihydroxy-derivatives, and considers it probable that whenever the hydroxy- and amido-groups are in the meta-position, this change can be effected easily. Further researches on other orcinols are promised.

V. H. V.

**Lutorcinol, an Isomeride of Orcinol.** By G. VOGT and A. HENNINGER (*Compt. rend.*, **94**, 650—652).—Monobromoparacresol is obtained by the action of bromine on a solution of paracresol (m. p.  $35^{\circ}$ ) in chloroform; it forms long colourless needles (m. p.  $17-18^{\circ}$ , b. p.  $218-220^{\circ}$ ). This is fused with potassium at  $200-210^{\circ}$ , and the fused mass neutralised and treated with ether in the usual way. The *lutorcinol*,  $C_6H_3Me(OH)_2$ , thus obtained forms small anhydrous colourless needles, m. p.  $104-105^{\circ}$ , readily soluble in water, alcohol, and ether, less soluble in chloroform and benzene. Exposed to air in presence of alkalis or alkaline carbonates, lutorcinol acquires a blood-red colour, turned to yellow by acids. A blood-red colour is also produced by calcium hypochlorite and potassium permanganate. Ferric chloride produces a deep dirty green colour, then a red-brown precipitate, which gradually acquires a deeper red tint, and contains no iron. These reactions are probably due to the presence of bromocatechol. Pure lutorcinol acquires only a faint red tinge in presence of alkalis and air. When treated with ammonia, in presence of air, it yields *lutorcein*, which has a brownish-yellow colour, changed by acids to pure yellow; it dyes yellow. When lutorcinol is heated with phthalic anhydride and sulphuric acid, it yields the corresponding phthalein, which has a yellow colour and an alkaline solution, and shows a beautiful green fluorescence, superior to that of fluorescein. Its bromo-derivative is red, and appears to resemble eosin.

When monobromoparacresol is fused with potash, a small quantity of protocatechuic acid is formed in addition to lutorcinol. Lutorcinol may also be obtained by fusing the potassium salt of paracresolsulphonic acid with potash, but the reaction requires a higher temperature ( $310-320^{\circ}$ ), and a greater proportion of protocatechuic acid is formed. Lutorcinol is probably identical with the *cresorcinol*, recently described by E. Knecht (preceding abstract).

This paper was contained in a sealed packet, deposited August 23rd, 1875. C. H. B.

**Phytosterin and Paracholesterin.** By O. HESSE (*Annalen*, **211**, 283—284).—Reinke and Rodewald (*Annalen*, **207**, 209) obtained a

mixture of cholesterin and parcholesterin from *Ethaliium septicum*, hence they regard the crystalline substance contained in peas, and to which the name of *phytosterin* has been given by the author (*ibid.*, 192, 175) as a mixture of these two bodies.

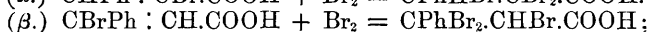
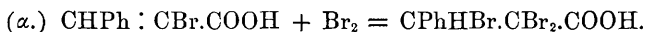
The author points out that the mode of preparation of phytosterin precludes the possibility of its being a mixture.

The results of the analyses of parcholesterin agree more closely with the formula  $C_{26}H_{46}O$  than with that proposed by Reinke and Rodewald,  $C_{26}H_{44}O$ .  
W. C. W.

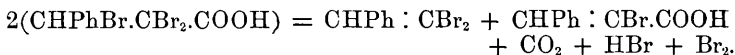
### An Aldehyde-ketone and a Glycol of the Aromatic Series.

By E. BURCKER (*Compt. rend.*, 94, 220—223).—From the products of a carefully-regulated action of chlorochromic acid on phenyl-propyl ketone, both dissolved in chloroform, the author separated the aldehyde-ketone,  $C_6H_5.CO.C_2H_4.CHO$ , a yellowish liquid (b. p.  $235^\circ$ ), soluble in alcohol, ether, chloroform, and benzene. It reduces silver nitrate, but does not combine with alkaline bisulphites. When this substance is heated with sodium-amalgam a thick yellowish liquid is produced (b. p.  $200^\circ$ ), which the author was able to recognise as a diatomic alcohol.  
R. R.

**Decomposition of Phenyltribromopropionic Acid.** By L. P. KINNICUT (*Amer. Chem. J.*, 4, 25—27). Glaser (*Annalen*, 143, 335 and 339), by treating  $\alpha$ - and  $\beta$ -bromocinnamic acids with bromine, obtained the two corresponding phenyltribromopropionic acids, thus:—



and Kinnicut finds that when  $\alpha$ -tribromophenylpropionic acid is placed in boiling water, and steam is passed into the liquid, the tribrominated acid is split up into dibromostyrene,  $\text{CHPh} : \text{CBr}_2$ , which passes over as a light yellow oil, and  $\alpha$ -monobromocinnamic acid, together with carbonic anhydride, hydrogen bromide, and free bromine:—



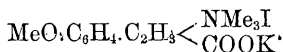
The author is continuing his investigation of these acids.

H. W.

**Elimination of Nitrogen from Tyrosine.** By G. KOERNER and A. MENOZZI (*Rendiconti del R. Istituto Lombardo* [2], 14, 521; *Gazzetta*, 1881, 549—550).—When methyl iodide and potassium hydroxide are added alternately to a solution of tyrosine in potassium methylate, using in all 5 mols. KOH and 5 mols. MeI to 1 mol. tyrosine, and assisting the action by a gentle heat, there is obtained a nearly colourless and perfectly neutral liquid, containing potassium iodide; an artificial alkaloid having considerable resemblance to the betaines, but differing therefrom by containing potassium as an essential constituent; also trimethylamine hydroxide; and the potassium-salt of methylparacoumaric acid.

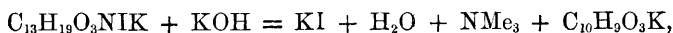
The alkaloid separated from the other bodies forms tabular and

prismatic crystals, colourless, hard, soluble in water, moderately soluble in hot, less so in cold alcohol. These crystals have the composition  $C_{13}H_{19}O_3NIK$ , and their products of decomposition (*infra*) show that their constitution may be represented by the formula,—



In fact, when heated on the water-bath with potash, they immediately give off trimethylamine, and are converted after some time into a white mass, composed of spherical groups of very minute needles, consisting of *potassium methyl-paracoumarate*,  $C_{10}H_9O_3K$ . The solution of this salt decomposed by hydrochloric acid, yields methyl-paracoumaric acid,  $C_{10}H_{10}O_3$ , in stellate groups of long shining needles, identical with the methyl-parahydroxyphenylacrylic acid which Perkin obtained synthetically from acraldehyde.

The preceding facts show: (1), that the decomposition of the alkaloid by potash may be represented by the equation:



which moreover is in accordance with the quantity of methyl-paracoumaric acid obtained; further (2) that tyrosine is one of the two possible alanines of hydroparacoumaric acid, and consequently that its synthesis should be effected by the action of ammonia on bromohydroparacoumaric acid, which contains the halogen in the lateral chain.

H. W.

### Monophenylboric Chloride and some of its Derivatives.

By A. MICHAELIS and P. BECKER (*Ber.*, 15, 180—185).—The authors have already made known (this Journal, 38, 395) the fact that monophenylboric chloride is produced by the action of mercury phenyl on boric chloride. When equal quantities of these reagents are heated at 180—200° for some time in sealed tubes, and the liquid portion is then poured off and distilled, *phenylboric chloride* passes over at 175° as a colourless oil, which solidifies in a freezing mixture to a crystalline mass melting at 0°. It is violently decomposed by water, but by conducting the decomposition slowly, *monophenylboric acid*,  $PhB(OH)_2$ , is formed. It crystallises in tufts of needles (m. p. 204°), sparingly soluble in cold, easily in hot water, and in alcohol and ether. It colours litmus only slightly red, is volatile with steam. Distilled by itself, it loses water, and phenylboric oxide,  $PhBO$ , passes over undecomposed. When the crystalline acid is left for some time in a desiccator, it undergoes a similar change. *Sodium phenylborate*,  $PhB(ONa)_2$ , crystallises in four-sided tablets easily soluble in water. *Calcium-hydrogen phenylborate*,  $(PhBO_2H)_2Ca$ , forms druses of colourless crystals. *Silver-hydrogen phenylborate*,  $PhBO_2HAg$ , is a yellow precipitate, which is soluble in ammonia, and changes on exposure to light. On heating it with water, it breaks up into silver oxide, benzene, and boric acid thus:  $2PhBO_2HAg + 3H_2O = Ag_2O + 2C_6H_6 + 2B(OH)_3$ . If excess of silver nitrate is added to phenylboric acid neutralised with ammonia and warmed, a silver mirror is deposited on the sides of the vessel. Mercuric chloride produces a glistening crystalline pre-

precipitate of mercuryphenyl chloride (m. p.  $250^{\circ}$ ). Phenylphosphoric acid,  $\text{PhPO}_3\text{H}_2$ , does not yield this body with mercury chloride. Physiologically phenylboric acid is a mild poison to mankind, but deadly to lower animals, e.g., frogs, bacteria, &c., it is hence a good antiseptic. *Phenylboric oxide* is prepared as described above, and is also obtained as a bye-product in the preparation of phenylboric chloride. It is a colourless crystalline mass (m. p.  $190^{\circ}$ ; b. p.  $360^{\circ}$ ), insoluble in water, but on prolonged boiling it is converted into phenylboric acid, which dissolves. *Ethyl phenylborate*,  $\text{PhB}(\text{OEt})_2$ , is formed when phenylboric chloride is mixed with excess of absolute alcohol: it is a colourless, pleasant-smelling liquid (b. p.  $176^{\circ}$ ), which is easily converted into phenylboric acid by moisture. Zinc ethide simply removes the phenyl from the alkyl salt, producing boron triethide. *Paratolylboric chloride*,  $\text{Me.C}_6\text{H}_4.\text{BCl}_2$ , is prepared by the action of boric chloride on mercuryditolyl in a similar way to the phenyl derivative. It forms a colourless crystalline mass (m. p.  $27^{\circ}$ ); it is violently decomposed by water, producing *tolylboric acid*,



This forms slender needles (m. p.  $240^{\circ}$ ), sparingly soluble in cold, very easily in hot water. With mercuric chloride, it yields a white precipitate of *mercurytolyl chloride*,  $\text{C}_7\text{H}_7\text{HgCl}$ . D. A. L.

**Carbostyryl.** By P. FRIEDLAENDER and H. OSTERMAIER (*Ber.*, **14**, 332—338).—A continuation of the author's former researches (this vol., 201). By the oxidation of oxycarbostyryl with alkaline permanganate, besides orthonitrobenzoic acid and water, there is also obtained *carbostyrylic acid*.

The latter crystallises in delicate white needles, sparingly soluble in cold water, easily soluble in hot water and alcohol; it melts at  $200^{\circ}$  with decomposition, and even at  $100^{\circ}$  it gives off carbonic anhydride slowly. By heating it with dilute hydrochloric acid, or with soda solution, carbostyrylic acid is decomposed into anthranilic and oxalic acids, thus:  $\text{C}_9\text{H}_5\text{NO}_6 = \text{C}_7\text{H}_7\text{NO}_2 + \text{H}_2\text{C}_2\text{O}_4$ ; it must thus be regarded as an oxalylanthranilic acid,  $\text{C}_6\text{H}_4(\text{NH.CO.COOH})\text{COOH.H}_2\text{O}$ , or more probably,  $\text{C}_6\text{H}_4\text{NHC}(\text{OH})_2(\text{COOH}).\text{COOH}$ . By the action of phosphorus pentachloride on carbostyryl or oxycarbostyryl monochloroquinoline is obtained, which forms long needles (m. p.  $37^{\circ}$ , b. p.  $267^{\circ}$ ); in its chemical and physical properties it is intermediate between dichloroquinoline and quinoline. It possesses strongly basic properties, forms a platinumchloride  $(\text{C}_9\text{H}_6\text{NCl.HCl})_2.\text{PtCl}_4 + 2\text{H}_2\text{O}$ , crystallising in needles. By nascent hydrogen, it is converted into tetrahydroquinoline, identical with that obtained from quinoline. On heating monochloroquinoline in sealed tubes with water, it is converted into carbostyryl.

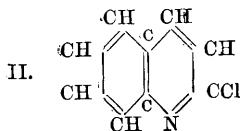
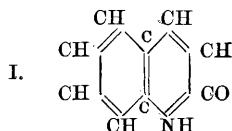
When monochloroquinoline is heated with alcoholic potash, it is converted into ethylcarbostyryl,  $\text{C}_9\text{H}_5\text{NOEt}$ , a sweet, colourless oil (b. p.  $206^{\circ}$ ) easily soluble in dilute acids; it is identical with the product of the action of ethyl iodide on sodium carbostyryl. When heated with hydrochloric acid, it is decomposed into carbostyryl and ethyl chloride; it is converted by sodium-amalgam into *dihydroethyl car-*



*bostryl*, which crystallises in needles having a silvery lustre and melting at  $199^{\circ}$ . Similarly methylcarbostyryl, an oil smelling like oranges (b. p.  $247^{\circ}$ ), and phenylcarbostyryl, crystallising in glistening leaflets (m. p.  $69^{\circ}$ ), are described.

Weinberg has shown that a monochlorethylcarbostyryl is obtained from dichloroquinoline. On heating this with hydrochloric acid, it is converted into *monochlorocarbostyryl* (m. p.  $24^{\circ}$ ), which is analogous in its physical properties to carbostyryl.

The conversion of monochloroquinoline into carbostyryl cannot readily be explained if the structural formula of carbostyryl be I—



and if chloroquinoline has the constitution represented above (II); but this difficulty disappears if carbostyryl be considered to be a hydroxyquinoline, although this hypothesis involves some difficulty in explaining the formation of carbostyryl from amidocarbostyryl (cf. Abstr., 1881, 598).  
V. H. V.

#### Action of Iodine on Naphthalene at High Temperatures.

By A. BLEUNARD and G. VRAU (*Compt. rend.*, **94**, 534—536).—30 parts iodine were heated with 70 parts naphthalene in a sealed tube at  $250^{\circ}$  for 12 hours. The black product thus obtained was boiled with potash to remove excess of iodine, and finally washed with warm water. The black powder contains iodine in combination, and when heated gives off violet vapours and hydriodic acid. Alcohol and carbon bisulphide dissolve mere traces, but benzene dissolves a much greater quantity, forming a strongly dichroic liquid, red by transmitted, and green by reflected light. The thick liquid left on evaporation of the benzene may be separated by means of ether into a thick red liquid, soluble in ether, of the composition C, 81.0; H, 6.9; O, 12.1 = 100.0, and a reddish powder, much less soluble in ether, of the composition, C, 88.4; H, 5.7; O, 5.9 = 100. The two bodies could not be perfectly separated.

The residue left after treatment with alcohol, carbon bisulphide and benzene, constitutes more than 90 per cent. of the total product, and has the composition: C, 75.2; H, 3.8; I, 21.4 = 100, agreeing with the formula  $C_{40}H_{23}I$ , or assuming that the iodine replaces one atom of hydrogen,  $C_{40}H_{24} = 4C_{10}H_6$ .—The principal action of the iodine on the naphthalene is the removal of hydrogen in the form of hydriodic acid, with formation of the body  $x C_{10}H_6$ .  
C. H. B.

**Dimethylnaphthalene.** By A. EMMEDT and F. REINGRUBER *Annalen*, **211**, 365—371).—The authors have shown (*Annalen*, **206**, 367 and 372) that the portion of coal-tar oil which distils between the boiling points of naphthalene and acenaphthalene contains methylnaphthalene (b. p.  $242^{\circ}$ ). By repeated redistillation of the hydro-

carbons boiling between  $250^{\circ}$  and  $280^{\circ}$ , a mixture of several isomeric dimethylnaphthalenes is obtained (b. p.  $250-270^{\circ}$ ).

The mixture yields a crystalline picrate. The barium salt of the dimethylnaphthalene-monosulphonic acid is easily soluble in water.

W. C. W.

**Dichloronaphthalene and Chloronaphthol from  $\beta$ -Naphthol-sulphonic Acid.** By A. CLAUS and M. DEHNE (*Ber.*, **15**, 319—322). The authors have confirmed Alén's researches (this vol., 409) on the dinitrochloronaphthalene and the monochlorophthalic acid obtained from the so-called  $\epsilon$ -dichloronaphthalene.

The neutral alkali salts of the chlorophthalic acid are readily soluble in water; the potassium salt forms large acicular crystals; the silver salt forms a white stable precipitate. The chloro- $\beta$ -naphthol from  $\beta$ -naphtholsulphonic acid (Abstr., 1811, 981) gives the same chlorophthalic acid as that mentioned above. These facts lead to the conclusion either that by the oxidation of the dichloronaphthalene the chlorine atom which has taken the place of the sulphy-group of the  $\beta$ -naphthol-sulphonic acid is unattacked, and remains in the chlorophthalic acid, or that in the dichloronaphthalene, and in the chloro- $\beta$ -naphthol, as in the  $\beta$ -naphtholsulphonic acids, both the substituting groups are in the  $\beta$ -position, one in each benzene nucleus. The author inclines to the latter view.

In conclusion, a comparison is drawn between  $\alpha$ - and  $\beta$ -naphthol-sulphonic acids; the former gives baric salts readily, the latter only with difficulty; with nitric acid, the former yields dinitronaphthol, the latter a nitrosulphonic acid; the former is converted into dichloronaphthoquinone by potassium chlorate and hydrochloric acid, the latter is for the most part unattacked by these reagents.

V. H. V.

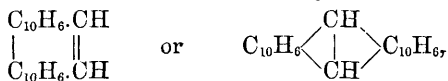
**Naphthalene-Derivatives.** By I. GUARESCHI (*R. Accad. d. Scienze di Torino*, **16**, 568—570; *Gazzetta*, 1881, 542).—This paper is a sequel to the short note on the bromo- and bromonitro-naphthalenes published by the author in 1877 (this Journal, **31**, 712). Having prepared a large quantity of dibromonaphthalene by Glaser's method, he has obtained from it the following compounds:—(1) Glaser's dibromonaphthalene melting at  $81-82^{\circ}$ . (2) From the mother-liquors of this, products melting at  $67-70^{\circ}$ , and from these a dibromonaphthalene melting at  $67.5-68^{\circ}$ , identical with the  $\beta$ -dibromonaphthalene (m. p.  $70-71^{\circ}$ ), which he obtained in 1877. (3) Another dibromonaphthalene of Glaser, said to melt at  $76^{\circ}$ , whereas Jolin separated from the last mother-liquors a dibromonaphthalene melting at  $60-61^{\circ}$ , whence Guareschi is of opinion that Glaser's compound melting at  $76^{\circ}$  was a mixture of the dibromonaphthalenes melting respectively at  $81-82^{\circ}$  and at  $68^{\circ}$ . By oxidation of a dibromonaphthalene, there is also obtained the anhydride of a bromophthalic acid (m. p.  $207.5-208^{\circ}$ ).

As secondary products of the preparation of monobromonaphthalene by the action of bromine in the cold on naphthalene dissolved in carbon sulphide, there are obtained: the dibromonaphthalene melting at  $81-82^{\circ}$ , which is likewise formed by the action of bromine-vapour on naphthalene; another melting at  $68^{\circ}$ , and a third (discovered by Wichelhaus and Darmstadter) at  $126-127^{\circ}$ .

The author has further obtained a new monobromonitronaphthalene in beautiful yellow needles melting at  $127.5^{\circ}$ . H. W.

**A Diatomic Alcohol Derived from  $\beta$ -Naphthol.** By G. ROUSSEAU (*Compt. rend.*, **94**, 133—136).—By treating  $\beta$ -naphthol with chloroform in presence of but a small excess of caustic soda solution, the author obtained, besides the aldehyde indicated by theory, a white crystalline substance, amounting to 40 per cent. of the naphthol employed. It is almost insoluble in benzene, carbon bisulphide, and acetic acid, but sparingly soluble in ether and light petroleum. It is insoluble in alkalis, but when warmed with sulphuric acid, it yields a blood-red liquid with a splendid green fluorescence.

The diatomic character of the alcohol is established by the analysis of the diacetate and the ether, and a study of its oxidation-products will show whether it is derived from the hydrocarbon—



Its transformations show that for the present the new alcohol must be ranked with the pseudo-glycols and particularly with the pinacones.

R. R.

**Action of Amines on the Quinones.** By T. ZANCKE (*Ber.*, **15**, 279—287).—A continuation of the author's researches (*Abstr.*, 1881, 595, 915).

$\beta$ -naphthaquinoneanilide differs from the corresponding  $\alpha$ -compound in behaving as a feeble monobasic acid; it is, however, converted into the  $\alpha$ -compound by heating it with alcohol, or with acetic or sulphuric acid. The author has examined the question whether the acid nature is due to a hydroxyl or the NH group, by the preparation of ethereal derivatives. If the hydroxyl group were present (a view which seems to be precluded by the impossibility of obtaining an acid radicle derivative) an ether of hydroxynaphthoquinone would be formed, but if the NH group were the cause of the acid function, a higher homologue of naphthaquinone would be formed by the substitution of a hydrogen-atom by a paraffinoid group. The author prepared some of these ethereal derivatives, but from want of material was unable to decide their constitution.

The methyl compound obtained from the silver salt of  $\beta$ -naphthaquinoneanilide and methyl iodide crystallises in golden needles (m. p.  $151^{\circ}$ ), the ethyl compound in glistening monoclinic prisms (m. p.  $104^{\circ}$ ), soluble in alcohol, benzene, and chloroform, the isopropyl compound in large golden crystals. These compounds are not saponified by the alkalis, and the author is at present investigating the action of acetic, sulphuric, and hydrochloric acid on them. By passing nitrous fumes into an alcoholic solution of the  $\beta$ -anilide, white crystalline needles separate out before the solution is saturated; subsequently a red crystalline substance is formed. The white compound is very unstable, losing the elements of alcohol, and yielding the red compound, which crystallises in long needles (m. p.  $245^{\circ}$ ). By reducing agents, it is converted into an indigo-blue compound, soluble in benzene, ether, &c.; it has feebly basic properties, but its salts do not

seem to be stable. With acetic anhydride, it yields an acetyl-derivative crystallising in golden-yellow leaflets; by oxidising agents, it is converted into a golden-yellow substance crystallising in leaflets or needles. As the constitutional formula of the naphthaquinoneanilide has not been satisfactorily established, the formulæ of these compounds cannot be well determined; it appears that the red compound is derived from the naphthoquinoneanilide by the replacement of H by NO, and has the formula  $C_{16}H_{10}(NO)NO_2$ ; the blue compound has the probable formula  $C_{16}H_{10}(NH_2)NO_2$ ; and the golden-yellow compound obtained by oxidation the formula  $C_{16}H_9(NH)NO_2$ . Further investigations are required to confirm these views.

The toluidines act on  $\beta$ -naphthaquinone like aniline; the paratoluidine compound can hardly be distinguished from the corresponding aniline compound; its alkali salts are easily soluble; its calcium, barium, mercury, silver salts are insoluble precipitates. With nitrous acid,  $\beta$ -naphthaquinone-paratoluide gives a red compound (m. p. 240—245°), and a blue reduction product, which yields an acetyl-derivative (m. p. 190°) and an oxidation product (m. p. 260—265°). Similar compounds were obtained from orthotoluidine. V. H. V.

**Naphthylsulphuric Acid.** By R. NIETZKI (*Ber.*, **15**, 305—306).—It has recently been shown that naphthol resembles the alcohols rather than the phenols in its reactions. By rubbing finely powdered dry  $\beta$ -naphthol with sulphuric acid, a rise of temperature takes place, and a crystalline substance separates out. On neutralisation with soda, delicate crystalline needles are obtained, soluble in water, sparingly soluble in alcohol. On acidifying an aqueous solution of these crystals with hydrochloric acid, they are decomposed into naphthol and sulphuric acid; this change characterises the compound as analogous to hydrogen ethyl sulphate. By indirect analysis the author shows that the acid has the formula  $C_{10}H_7SO_4H$ .

By heating a mixture of the sodium salt of this acid with sodium ethyl sulphate, ethyl  $\beta$ -naphthol is obtained; similarly  $\beta$ -dinaphthyl ether and other ethers may be formed. Naphthylsulphuric acid will not react with the diazo-compounds. V. H. V.

**Action of Phosphorus Pentachloride on  $\alpha$ -Naphtholsulphonic Acid.** By A. CLAUS and H. OEHLER (*Ber.*, **15**, 312—315).—The authors have examined the action of phosphorus pentachloride on  $\alpha$ -naphtholsulphonic acid under various conditions. The results differ most markedly from those obtained with the corresponding  $\beta$ -acid (*Abstr.*, 1881, 914), for there is formed neither an ethereal combination of the hydroxyl and sulphonic group nor an ethereal salt of phosphoric acid. When phosphorus pentachloride and anhydrous salts of  $\alpha$ -naphtholsulphonic acid are heated together at a temperature of 60—100° C.,  $\alpha$ -naphtholsulphonyl chloride is obtained; at 100—150° a *monochloronaphthol*,  $C_{10}H_7Cl(OH)$ , and a *dichloronaphthalene* are formed. These may be separated by distillation in a current of steam, when the chloronaphthol passes over first. It crystallises in small brick-red, interlaced needles (m. p. 57°), soluble in alcohol, ether, and chloroform; by oxidation with alkaline permanganate or excess of

concentrated nitric acid, it is converted into phthalic acid. With a small quantity of nitric acid, it yields naphthoquinone (m. p.  $125^{\circ}$ ).

Dichloronaphthalene crystallises in long, white needles (m. p.  $94^{\circ}$ ), soluble in alcohol and ether. Like the chloronaphthalene, it yields on oxidation phthalic acid and naphthaquinone.

In both compounds the hydroxyl-group and chlorine-atoms are in the position  $\alpha_1 : \alpha_2$ ; but the dichloronaphthalene differs from the  $\alpha_1\alpha_2$  dichloronaphthalene described by Beilstein, which yields dichlorophthalic acid on oxidation; this discrepancy the authors propose to examine further.

V. H. V.

**Essence of Linaloes.** By H. MORIN (*Compt. rend.*, **94**, 733—735).—By prolonged treatment with a saturated aqueous solution of hydrochloric acid, and exposure to light, essence of linaloes (*Licari kanali*, Abstr., 1881, 738), yields a hydrochloride which decomposes on distillation at ordinary pressure, but may be distilled with an excess of water under reduced pressure. It is a colourless optically inactive liquid of the composition  $C_{10}H_{16}, 2HCl$ , with an aromatic odour recalling that of camphor (sp. gr. at  $16^{\circ} = 1.069$ ). When distilled with calcium hydroxide, it yields a hydrocarbon,  $C_{10}H_{16}$ , a colourless, very mobile, optically inactive liquid, with a peculiar, slightly aromatic odour (b. p.  $168$ — $172^{\circ}$  at 765 mm.; sp. gr. at  $18^{\circ} = 0.835$ ). This hydrocarbon, for which the author proposes the name *licarene*, differs from citrene in its boiling point and specific gravity. It is readily converted into isomerides or polymerides by the action of heat or certain chlorides, such as zinc chloride. Essence of linaloes is therefore the hydrate of *licarene*, an isomeride of terebenthene.

A mixture of essence of linaloes, alcohol, and nitric acid, remains clear for some time, but gradually becomes turbid, and finally an upper layer of liquid separates out, which is insoluble in water, and is dextrogyrate, whereas essence of linaloes is lævogyrate.

C. H. B.

**Essence of Savory.** By A. HALLER (*Compt. rend.*, **94**, 132).—Essence of savory from *Satureia montana* is an orange-yellow rather thick liquid of sp. gr. 0.7394 at  $17^{\circ}$ . A solution of potash dissolves out one-fifth of the volume of the essence, and by appropriate treatment of the solution the author isolated a colourless liquid (b. p.  $232^{\circ}$ ) identical with the carvacrol which was obtained by Schweitzer from carvol derived from essence of cumin, and identical also with the  $\beta$ -thymol of Müller and Patt, with the hydroxycymene of Kekulé and Fleischer, &c. Essence of savory contains about 40 per cent. of carvacrol, as well as another phenol with a higher boiling point. The hydrocarbons which enter into its composition appear to be two terpenes boiling at  $172$ — $175^{\circ}$  and  $180$ — $185^{\circ}$  respectively.

R. R.

**Products of the Distillation of Colophony.** By A. RENARD (*Compt. rend.*, **94**, 727—730; see also this Journal, **40**, 738).—That portion of the product of the distillation of colophony which boils at  $154$ — $157^{\circ}$  is a mixture of two hydrocarbons,  $C_{10}H_{16}$  and  $C_{10}H_{18}$ , which cannot be separated by distillation. This mixture is lævogyrate, is

partially converted into a hydrochloride by the action of hydrochloric acid gas, and is violently attacked by bromine with formation of unstable dibromides. It is attacked by nitric acid of sp. gr. 1.2 at 80° with production of a resin which dissolves in the excess of acid. The solution will not crystallise, but yields a syrupy acid, which forms an insoluble lead salt. Fuming sulphuric acid partially converts the mixture into cymenesulphonic acid, which yields a barium salt identical with that obtained from the terebenthene boiling at 170—173° (*loc. cit.*).

If the mixture of the two hydrocarbons is treated with one-twentieth of its volume of ordinary sulphuric acid (sp. gr. 1.8), and the supernatant liquid distilled after 24 hours, it yields two fractions, one boiling below 200°, the other, consisting mainly of polymerides, above 300°. By several repetitions of this treatment on the portion boiling below 200°, with increasing quantities of sulphuric acid, a new hydrocarbon, *decine*,  $C_{10}H_{18}$ , is obtained. It is not attacked by ordinary sulphuric acid, hydrochloric acid, or by ordinary boiling nitric acid; but is dissolved by fuming nitric acid in the cold. Bromine is without action in the dark, but in daylight attacks it with evolution of hydrobromic acid. Fuming sulphuric acid dissolves it slowly, forming an acid which yields a non-crystalline barium salt. This hydrocarbon exists in the original mixture to the extent of about 7 per cent., a proportion too small to account for the properties of that mixture, which can only be explained by the assumption that it contains another hydrocarbon,  $C_{10}H_{18}$ , attacked by ordinary sulphuric acid.

If instead of heating the mixture with sulphuric acid of sp. gr. 1.8, it is repeatedly treated with acid of sp. gr. 1.75, it yields a mixture of *decine* and a new terebenthene, which forms a liquid monohydrochloride, and is produced by the action of the sulphuric acid on the original terebenthene. This second terebenthene is converted into cymenesulphonic acid by ordinary sulphuric acid. C. H. B.

**Dichlorocamphor.** By P. CAZENEUVE (*Compt. rend.*, **94**, 730—732).—Camphor is dissolved in absolute alcohol, and treated with a current of dry chlorine for several hours at 80—90°. Heat is developed and hydrochloric acid is given off in large quantity. The product is repeatedly treated with water, and then heated to remove chloral and hydrochloric acid. On cooling, it solidifies to a crystalline mass, which may be purified by crystallisation from alcohol. The *dichlorocamphor*,  $C_{10}H_{14}Cl_2O$ , thus obtained forms large white oblique prisms, slightly soluble in cold, but very soluble in hot alcohol; soluble in ether, in the vapour of which it liquefies, but insoluble in water. It softens at 89°, and melts at 93°, at which temperature it gradually volatilises without decomposition. Above 150°, it blackens and decomposes with evolution of hydrochloric acid. On continued heating, the temperature rises to 263°, at which point it remains constant, and a colourless liquid distils over.

The formation of the dichlorocamphor is probably preceded by that of the monochloro-derivative. No higher derivative is obtained by the prolonged action of chlorine at the temperature of the experiment.

C. H. B.

**Note on the Phenol obtained by the Action of Zinc Chloride on Bromocamphor.** By R. SCHIFF (*Gazzetta*, 1881, 532—533).—The author, in 1880, obtained by the action of zinc chloride on bromocamphor a liquid phenol boiling at  $226^{\circ}$  and exhibiting nearly the composition of a thymol. The quantity obtained was however very small, and the analyses not quite satisfactory; and though larger quantities have since been obtained, and submitted to fractional distillation, the author finds that all the fractions give percentages of hydrogen somewhat too low for phenols of the aromatic series with saturated lateral chains. The composition of the phenol above mentioned is still therefore undecided. H. W.

**Colouring Matter in Flour Paste.** By L. DE BOISBAUDRAN (*Compt. rend.*, 94, 562—563).—The violet pigment is contained in celluloses which grow near the surface of the paste. The paste containing the organism was placed in different atmospheres; acetic acid appeared the most efficacious in promoting the formation of the colouring matter. The pigment is insoluble in water, but dissolves in alcohol and ether. When dry it has a metallic lustre, similar to that of the aniline colours. Hydrochloric acid turns the violet alcoholic solution to blue or bluish-green, and finally decolorises it; sodium hydroxide changes it to green, which rapidly passes into yellow with a reddish tinge. The blue-violet alcoholic solution shows a nebulous absorption-band in the yellow, green, and greenish-blue, which extends as the thickness of the liquid layer is increased. C. H. B.

**Products of the Transformation of Quinoline.** By G. KOERNER (*Rendiconti del R. Istituto Lombardo* [2], 14, 401, 526; *Gazzetta*, 1881, 548—550).—When quinoline is heated with methyl iodide in molecular proportion, and the product is distilled with potash, a mixture is obtained, separable into two principal products boiling respectively at  $193^{\circ}$  and  $240^{\circ}$ . The former of these is dimethylaniline, and is converted by oxidation into an acid belonging to a special group, to which there is no known analogue. This acid is still under investigation.

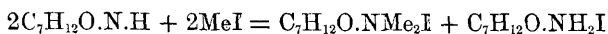
The second product, boiling at about  $240^{\circ}$ , is heavier than water, and gives by analysis numbers agreeing nearly with the formula of a methyl-quinoline; and in fact it exhibits all the properties of a lepidine, excepting that it has a more agreeable odour.

Finally the author states that he has obtained compounds possessing, like quinine, the power of lowering the temperature of the animal body, and amongst these he mentions, as of especial interest, the derivatives of a base  $C_8H_6N_2$ , the preparation of which will be described in a future communication. H. W.

**Tropine.** By G. MERLING (*Ber.*, 15, 287—293).—A continuation of the author's researches (this vol., 416). By the oxidation of tropine with alkaline permanganate a secondary base, *tropigenine*,  $C_7H_{13}NO$ , is formed, which readily combines with nitrous acid to give a nitroso-compound, and with methyl iodide reproduces tropine. The platinum-chloride crystallises in dark orange-coloured tables, sparingly soluble in

water, soluble in alcohol. By treating a hydrochloric acid solution of tropigenine with silver oxide, distilling, and subsequent subliming the product in a vacuum, the free base is obtained in the form of hard colourless needles (m. p.  $161^{\circ}$ ); it is easily soluble in water and alcohol, and absorbs carbonic anhydride from the air with avidity.

The *aurochloride* crystallises in golden-yellow leaflets, sparingly soluble in cold water. By the action of methyl iodide on tropigenine there are formed the hydriodides of tropigenine and tropine, together with methyltropine iodide, thus:—



and  $\text{C}_7\text{H}_{12}\text{ONH} + \text{MeI} = \text{C}_7\text{H}_{12}\text{O.NHMeI}$ . These results confirm former experiments which have established the presence of a methyl-group in tropine. By oxidising tropine with chromic acid, a dibasic acid,  $\text{C}_6\text{H}_{11}\text{O}(\text{COOH})_2$ , is obtained, which gives off a molecule of carbonic anhydride at  $220\text{--}240^{\circ}$ . This acid will combine with both acids and bases; its hydrochloride forms well crystallised double salts with platinic and gold chlorides. The author has prepared the barium, lead, and other salts of this acid, and proposes to investigate further its reactions and constitution.

V. H. V.

**Researches on Atropine.** By L. PESCI (*Accad. dei Lincei*, 9, 147; *Gazzetta*, 1881, 538—539).—In a former paper (Abstr., 1881, 293) the author mentioned the formation of a basic substance by the action of nitric acid on atropine; and he now gives further directions for its preparation and describes its properties. This base crystallises in colourless inodorous prisms; melts at  $60\text{--}62^{\circ}$ ; is slightly soluble in water, more soluble in light petroleum and amyl alcohol, very slightly in common alcohol, ether, chloroform, benzene, carbon sulphide, and methyl alcohol. Its taste is bitter and disagreeable. Its analysis leads to the formula  $\text{C}_{17}\text{H}_{21}\text{NO}_2$ , differing from that of atropine,  $\text{C}_{17}\text{H}_{23}\text{NO}_3$ , by  $\text{H}_2\text{O}$ , whence the author proposes to call it apoatropine, and concludes that, in its formation, the nitric acid plays the part of a dehydrating agent. The *sulphate*,  $\text{C}_{17}\text{O}_{21}\text{NO}_2, \text{SO}_4\text{H}_2 + 5\text{H}_2\text{O}$ , forms very beautiful nacreous laminar crystals; the *hydrochloride*, *nitrate*, *hydriodide*, *chromate*, and *acetate* have also been prepared.

When apoatropine (10 g.) is heated at  $120\text{--}130^{\circ}$  in sealed tubes with fuming hydrochloric acid (60 g.) for four hours, it is decomposed, with deposition of a brown semi-fluid stratum; and on decanting the supernatant acid liquid, and dissolving the brown substance in dilute sodium carbonate, two liquids are again formed, one acid, the other alkaline, containing the products of the reaction. On exhausting the acid liquid with ether and evaporating the ether, a crystallised base is obtained which melts at  $60\text{--}61^{\circ}$ , and appears, from its reactions and the analysis of its platinochloride, to consist of tropine. The alkaline liquid yields a white pulverulent substance which melts at  $196\text{--}198^{\circ}$ , crystallises from alcohol on addition of water, and is shown by its reactions and analysis to consist of isotropic acid,  $\text{C}_9\text{H}_8\text{O}_2$ . The acid ethereal liquid resulting from agitating the hydrochloric acid solution with ether yields on evaporation a confusedly



crystallised substance, which dissolves in benzene, crystallises therefrom by slow evaporation in transparent tablets melting at  $104-106^{\circ}$ , dissolves sparingly in cold water, and appears from its analysis and its reactions to be a tropic acid,  $C_9H_8O_2$ .

The constitutional formula of apoeatropine may be derived, according to the author, from that of atropic acid,  $CH_2 : CPh.CO.OH$ , by substituting for the carboxylic hydroxyl the univalent radicle  $C_8H_4NO$ , giving for apoeatropine the formula  $CH_2 : CPh.CO.C_8H_4NO$ .

The following are the results of physiological experiments made by G. Malagola with apoeatropine on frogs, dogs, and men; 1. Apoeatropine neither dilates the pupil nor produces any other effect on the eye, beyond slight local irritation. 2. It perceptibly slackens the beating of the heart. 3. In moderately large doses, it produces characteristic chronic convulsions; in larger doses, rapid and violent convulsions. 4. The symptoms of poisoning quickly disappear.

H. W.

**Pathological Bases.** By SELMI (*R. Accad. dei Lincei*, 5, 174, 243; *Gazzetta*, 1881, 546—547).—The author, suspecting that, in various diseases, there are formed in the tissues, substances of poisonous nature, which, together with the alteration of the tissues, or by their sole action, determine the death of the patient, has analysed the urine of patients affected with progressive paralysis, miliary fever, rheumatic tetanus, and other diseases, also the urine of the insane, and finds that in all these cases, as in the animal body after death, bases are formed possessed of poisonous properties. The urine of a patient affected with progressive paralysis accompanied by increasing imbecility, yielded: 1. A base very much like nicotine but not identical therewith, having a specific poisonous action, especially on the spinal marrow, destroying its activity, and diminishing the general sensibility, the respiration, and the pulsations of the heart. 2. Another base, but in much smaller quantity, having the odour of conine. A base having the same odour, also in very small quantity, was extracted from the urine of a patient affected with rheumatic tetanus. From the urine of other patients, and from the blood and viscera of a mare, various other bases were extracted, of somewhat indefinite character, but all possessed of poisonous properties. The urine of a scorbutic patient yielded a white crystalline substance, of which the part soluble in alcohol possessed the power of converting starch into glucose.

H. W.

**Researches on the Formation of Ptomaines.** By E. PATERNO and P. SPICA (*Gazzetta*, 1882, 63—82).—The experiments recorded in this paper were made with the view of ascertaining whether substances identical with, or similar to, the bases called *ptomaines* or *cadaveric alkaloids*, can be extracted from animal fluids in their normal state, before they enter into putrefaction. The liquids experimented on were fresh blood and fresh egg-albumin, acidulated solutions of which were tested with various reagents commonly used for the detection of alkaloids, *e.g.*, phosphomolybdic acid, potassio-mercuric iodide, palladious chloride, auric chloride, mercuric chloride, tannic acid, &c.—with the result of showing that the reactions thus obtained are exactly

similar to those produced by the same reagents in solutions of the so-called ptomaines extracted from the dead animal body.

With reference to the search for poisonous alkaloids in a dead body by the hypodermic injection of fluids extracted therefrom into the body of a living animal, the authors point out the necessity of ensuring that the fluids so injected are free from infective germs, as otherwise it would not be safe to infer that any poisonous effects that may result from their injection are really due to the presence of alkaloids.

H. W.

**The Quebracho Drugs from the Argentine Republic.** By O. HESSE (*Annalen*, **211**, 249—282).—Not only the amount of alkaloids, but also the number of different bases, contained in the bark of "Quebracho blanco" (*Aspidosperma Quebracho*) varies according to the different sources from which the bark is obtained. No fewer than six alkaloids are contained in the bark from Pilciao in the Argentine Republic. The alkaloids are obtained by boiling the bark in alcohol. The alcoholic solution is evaporated, soda is added to the residue, and the mixture is extracted with ether or chloroform. This extract is evaporated to dryness, the residue dissolved in dilute sulphuric acid, and the alkaloids precipitated from the acid solution by the addition of caustic soda. On recrystallisation from a small quantity of boiling alcohol, a mixture of *Aspidospermine*,  $C_{22}H_{30}N_2O_2$ , and *quebrachine*,  $C_{21}H_{26}N_2O_3$ , is deposited; *aspidospermatine*, *aspidosamine*, and *hypoquebrachine* are contained in the mother-liquor. The crystalline deposit is dissolved in alcohol and mixed with hydrochloric acid; on evaporating the solution, quebrachine hydrochloride crystallises out. The aspidospermine in the filtrate is precipitated by ammonia and purified by recrystallisation from alcohol: this alkaloid forms colourless prisms and needles (m. p.  $206^\circ$ ), freely soluble in absolute alcohol, benzene, and chloroform. The alcoholic solution is laevogyrate. The pure alkaloid gives a magenta coloration with perchloric acid, and possesses the properties ascribed to it by Fraude (*Ber.*, **11**, 2189; **12**, 1560). It is a very weak base, forming amorphous salts, which, when treated with chloroform, lose a portion of the base.

*Aspidospermatine*,  $C_{28}H_{28}N_2O_2$ .—The bases contained in the mother-liquor obtained in the preparation of aspidospermine, are converted into acetates. Sodium bicarbonate is added to the mixture, and the precipitate produced removed by filtration. To the clear liquid, a small quantity of ammonia is added to remove the aspidosamine. The filtrate is mixed with soda and extracted with ether. The residue which remains on evaporating the ethereal extract is treated with light petroleum, which dissolves aspidospermatine, but leaves hypoquebrachine undissolved. The aspidospermatine is washed with alcohol and again recrystallised from light petroleum.

The pure alkaloid forms delicate needle-shaped crystals (m. p.  $162^\circ$ ), soluble in alcohol, ether, and chloroform.  $[\alpha]_D = -72.3$  for a 2 per cent. alcoholic solution at  $15^\circ$ . Aspidospermatine resembles aspidospermine in its behaviour with perchloric acid and ferric chloride. Aspidospermatine combines with acids, forming amorphous salts. Alkalis produce white precipitates (soluble in pure water) with the solutions of these salts. On the addition of sodioplutinic

chloride to the hydrochloride, a pale yellow precipitate is thrown down, which has the composition  $(C_{22}H_{26}N_2O_2)_2, PtCl_6H_2 + 4H_2O$ .

The precipitate of crude *aspidosamine* mentioned above is dissolved in acetic acid, reprecipitated by ammonia, and is freed from traces of the other alkaloids by washing with light petroleum.

Aspidosamine is almost insoluble in water, but dissolves freely in ether, chloroform, alcohol, and benzene. The alcoholic solution has an alkaline reaction. It neutralises acids, forming amorphous salts. The aqueous solution of the hydrochloride gives a brownish-red coloration with ferric chloride. The platinochloride has the composition  $(C_{22}H_{26}N_2O_2)_2, PtCl_6H_2 + 3H_2O$ . Aspidosamine gives a blue coloration with a mixture of sulphuric and molybdic acids, a dark blue colour with sulphuric acid and potassium dichromate, and a magenta coloration on boiling with perchloric acid.

The crude *hypoquebrachine*, obtained in the separation of aspidospermamine (*vide supra*), is dissolved in acetic acid. The solution is treated with animal charcoal, saturated with sodium hydroxide, and extracted with ether. The extract, on evaporation, leaves the hypoquebrachine,  $C_{21}H_{26}N_2O_3$ , in the form of an amorphous mass (m. p.  $80^\circ$ ). The alkaloid is soluble in alcohol, ether, and chloroform. It is a powerful base, forming yellow amorphous salts, which dissolve freely in water. The aqueous solution of the hydrochloride gives a cherry-red coloration with ferric chloride, a yellow precipitate which rapidly changes to violet with chloride of gold, and a pale yellow amorphous precipitate with sodium platinum chloride. The platinochloride has the composition  $(C_{21}H_{26}N_2O_2)_2, PtCl_6H_2 + 4H_2O$ .

Crude *quebrachine* can be purified by recrystallising the hydrochloride or sulphate. The alkaloid is precipitated from an aqueous solution of its salts by soda, and the precipitate is recrystallised from alcohol. Pure quebrachine,  $C_{21}H_{26}N_2O_3$ , crystallises in colourless needles, which melt with partial decomposition at  $215^\circ$ . The crystals dissolve freely in chloroform and in boiling alcohol: these solutions deflect the ray of polarised light to the right. For a 2 per cent. solution in alcohol  $[\alpha]_D = +62.5$  at  $15^\circ$ , and in chloroform  $[\alpha]_D = +18.6^\circ$ . The tests for this alkaloid, and a description of some of its salts have been previously given by the author (*Ber.*, **13**, 2308; this *Journal*, 1881, Abstr., 294). The neutral *oxalate* crystallises in needles, insoluble in alcohol or water. The *tartrate*,



forms colourless plates, soluble in water. The *citrate* crystallises in needles, soluble in hot water. The *hydriodide* is an amorphous body; the *thiocyanate* is crystalline.

*Quebrachamine*.—The mother-liquors obtained in the purification of aspidospermamine by recrystallisation from alcohol, deposit crystals of aspidospermamine on spontaneous evaporation; on further evaporation an amorphous residue remains, from which quebrachamine can be extracted by treatment with a small quantity of boiling alcohol. The alkaloid is deposited in colourless plates (m. p.  $142^\circ$ ) on the addition of water to the alcoholic solution. Quebrachamine dissolves readily in alcohol, benzene, chloroform, and ether. The alcoholic

solution is strongly alkaline, and has an intensely bitter taste. With sulphuric acid and molybdic acid or potassium dichromate, quebrachamine gives a dark violet coloration. Alkalis produce a white precipitate with solutions of quebrachamine salts. The hydrochloride is amorphous. Quebrachamine has only been met with in one sample of quebracho bark. Its composition has not yet been ascertained.

The physiological action of these alkaloids has been previously described (*loc. cit.*).

In addition to these alkaloids, the bark also contains a neutral substance to which the name *Quebrachol* has been given. It is obtained by evaporating the ethereal extract of the bark, and treating the residue with a small quantity of hot alcohol; the alcoholic solution, on cooling, deposits colourless crystalline plates (m. p.  $125^{\circ}$ ) of quebrachol,  $C_{20}H_{34}O$ . The crystals dissolve freely in ether, chloroform, benzene, and acetone. Quebrachol resembles phytosterine in its colour reactions with sulphuric acid, but is less refractive than the latter compound.  $[\alpha]_D = -29.3$  for a 4 per cent. solution of quebrachol in chloroform at  $15^{\circ}$ . *Acetyl-quebrachol*,  $C_{20}H_{33}OAc$ , resembles quebrachol in crystalline form. It is less soluble than quebrachol in hot alcohol, but dissolves freely in ether, benzene, and light petroleum.

II. The bark of *Quebracho colorado* (*Loxopterygium Lorentzii*) contains small quantities of two alkaloids, which may be extracted by the method described at the beginning of this paper. On the addition of potassium thiocyanate to the mixed acetates, one of the alkaloids is precipitated. The second, to which the name *loxopterygine* has been given, is precipitated by adding ammonia to the filtrate. It is a white amorphous substance (m. p.  $81^{\circ}$ ), soluble in ether, alcohol, chloroform, benzene, and acetone. The solutions have an alkaline reaction and an intensely bitter taste. It gives a blood-red coloration with nitric acid, and a violet colour with a mixture of sulphuric and molybdic acids. Loxopterygine probably has the composition  $C_{26}H_{34}N_2O_2$ .

The alkaloid precipitated by potassium thiocyanate is an unstable compound. Its composition has not yet been ascertained.

W. C. W.

**Pilocarpine.** By CHASTAING (*Compt. rend.*, **94**, 223).—By treating pilocarpine with fused potash, the author obtained a volatile base which gave a precipitate with platinum chloride. This proved to be methylamine, and there was no evidence of the formation of any conicine. An examination of the residue seemed to show that, under the influence of the potash, the pilocarpine was split up into methylamine, carbonic anhydride, butyric acid, and traces of acetic acid.

R. R.

**Active Principles of Buxus Sempervirens.** By P. E. ALESSANDRI (*Gazzetta*, 1882, 96—108).—The chemical constituents of the bark of the box-tree have been examined by Fauré, Pavia, and Barbaglia\* with the result of demonstrating the existence therein of

\* See *Watts's Dictionary of Chemistry*, **1**, 699; **6**, 255; **8**, 365.

two alkaloids called *buxine* and *parabuxine*, neither of which however was obtained in the pure state, but only in the form of dark yellow resinous mixtures, not admitting of purification. The author of the present paper finds that better results are obtained by the use of oxalic acid; and by operating with this reagent on the fresh leaves, and on the bark and twigs, he has obtained three distinct alkaloids, viz., *buxeine* from the leaves, *buxine* from the bark, and *parabuxine* from both, but the largest quantity from the bark. Buxine and buxeine do not differ greatly in their properties, and may perhaps prove, on further examination, to be identical, but parabuxine is certainly a distinct substance; it is, perhaps, of acid nature, as it adheres tenaciously to the buxine, which is the chief constituent of the bark.

The following are the distinguishing physical and chemical characters of the three bodies:—

	Buxine.	Buxeine.	Parabuxine.
When heated ....	White.	Yellowish-white.	Purple-red.
Structure .....	Crystalline.	Crystalline.	Amorphous resin.
Solubility .....	Slightly soluble in water, moderately in alcohol, readily in ether.	Soluble in alcohol and ether; slightly in water.	Easily soluble in water and in alcohol; insoluble in ether.
Reactions:—			
with pure nitric acid.	Fine purple - red (very delicate reaction).	Greenish - yellow, changing in a few minutes to brick-red.	Greenish-yellow, not changing to red.
with sulphuric acid	Brick-red.	Blood-red.	Greenish-yellow, becoming dark.
with chromic acid mixture.	In the cold, a canary-yellow precipitate, forming a green aureola on heating, then dispersing.	Orange - coloured precipitate, which dissolves on heating, the liquid assuming a fine green colour.	Coloration, but no precipitate. Grass-green aureola on heating.

The fact that buxine is constantly coloured red by nitric acid, whereas with buxeine, this effect takes place after a few seconds only, seems to indicate that buxine is directly converted by nitric acid into parabuxine, and buxeine first into buxine, then into parabuxine.

Buxine has been found to act, like quinine, as a remedy for intermittent fever.

For the details of the preparation of the three bases, which are very lengthy, the original paper must be consulted. H. W.

**Myosin, its Preparation, Properties, Conversion into Syntonin, and Regeneration from the same.** By A. DANILEWSKY (*Zeitsch. f. Physiol. Chem.*, 5, 158—184).—*Preparation of Myosin.*—

The author uses for this purpose a 12 per cent. or 15 per cent. solution of ammonium chloride, in which the finely divided flesh is stirred, having previously been thoroughly washed with water. After several hours, it is strained and then filtered through paper, and the solution allowed to fall drop by drop into a tall vessel filled with distilled water. In this way the myosin separates in small flocks. Myosin prepared in this way combines with hydrochloric acid in various proportions. Myosin from rabbit's muscle required 3.12 per cent. hydrochloric acid, from calf's muscle 4.87 per cent. hydrochloric acid, from ox flesh 3.41 per cent. to 4.08 per cent. hydrochloric acid. It contains lime, magnesia, and phosphoric acid—these may be detected in the ash. If myosin be boiled in 50 per cent. alcohol and filtered hot, the extract will be perfectly clear when cold. If a concentrated solution of myosin is evaporated by heat, the clear fluid which separates contains a considerable quantity of calcium. Myosin is attacked rapidly by an acid pepsin solution and completely dissolved: an alkaline solution of pepsin on the other hand acts on it but slowly and incompletely. The conversion of myosin into syntonin by hydrochloric acid is rapid only when the hydrochloric acid is in considerable excess. One-half the hydrochloric acid necessary to combine with the myosin will suffice to dissolve it, but the author found that in such a solution a large quantity of the myosin remained unchanged even after a week.

*Syntonin.*—The formation of syntonin from myosin by hydrochloric acid is easy, but takes place only under well-defined conditions of temperature and quantity of acid. A solution of myosin in a very small quantity of hydrochloric acid is readily converted into syntonin on heating to 50° or 55°. The ash of syntonin has no alkaline reaction, and the watery extract contains no lime. The acid appears to remove the lime in solution in the process of conversion of myosin into syntonin. Syntonin is insoluble in a solution of ammonium chloride, and appears to combine with acids, although to a less extent than myosin.

*Insoluble Forms of Myosin and Syntonin.*—If the myosin is treated for a long time with distilled water, it gradually becomes insoluble in ammonium chloride solution, and its ash yields no lime salts when treated with water. The substance produced is, however, not syntonin, as it is insoluble in lime-water. It combines with hydrochloric acid, although to a less degree than myosin, and less also than the syntonin prepared from it (*i.e.*, the insoluble myosin). It dissolves slowly in 1 per cent. solution of soda, and if the solution is carefully neutralised, the precipitate exhibits the same properties as before, but if the solution in alkali be warmed for half an hour or an hour to 35° C. or 45° C., normal syntonin will be precipitated on acidification.

*Chemical Changes in the Conversion of Myosin.*—The hydrochloric acid cannot be combined with the lime present, as the quantity of the latter is far from sufficient to be accounted for in this way. According to the author, it is more probably associated with the amido-group in the myosin molecule. As a proof of this, the author adduces the platinochloride, which contains 7.26 per cent. chlorine. The calcium is considered by the author as combined with an inosite-

group in the myosin molecule, whose existence he demonstrated by its behaviour with trypsin, and also directly by the use of Scherer's reaction. The reactions and properties of these varieties of myosin and syntonin are set out in a table in the original.

*Conversion of Syntonin into Myosin.*—Syntonin is dissolved in lime-water; dry powdered ammonium chloride is added to saturation; the mixture is then filtered, and the alkaline, opalescent, thick solution neutralised cautiously with acetic acid until litmus-paper shows no alkaline reaction. This solution behaves exactly like a freshly prepared solution of myosin in sal-ammoniac. On dropping it into water, myosin is precipitated, the ash of which has an alkaline reaction, and yields lime to water. W. N.

**Compounds of Copper with Albumin.** By F. HARNACK (*Zeitschr. f. Physiol. Chem.*, 5, 198—210).—Neutral solutions of egg-albumin were treated with a solution of a simple copper salt so long as any precipitate was formed. The mixture was then neutralised with sodium carbonate. The precipitate could be washed without decomposition, and was of a clear blue-green colour, and very bulky, soluble with difficulty in excess of albumin and of the copper salt, readily soluble in acids and alkalis, forming with the latter a deep violet-coloured solution. By careful neutralisation, the compound could be again precipitated either from the acid or alkaline solutions, and this afforded a ready means of purification. When so prepared, the compound contained between 1.35 and 2.64 per cent. Cu. The former figure agrees with Rose's for copper albuminate, and the latter with other authorities if 1 per cent. is deducted for ash.

The author obtained, as the result of elementary analysis, the formulæ  $C_{204}H_{320}N_{52}O_{66}S_2Cu$  and  $C_{201}H_{318}N_{52}O_{66}S_2Cu_2$  for the two compounds respectively, *i.e.*, in the formula of egg-albumin 2 and 4 atoms of hydrogen respectively have been replaced by copper. The platinum compounds at present known agree very closely with this formula. How it is that under some circumstances one compound, and under others the other is formed, has not been determined. W. N.

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## Physiological Chemistry.

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### Elimination of Gaseous Nitrogen from the Animal Body.

By M. v. PETTENKOFER and C. VOIT (*Zeitschr. f. Biol.*, **16**, 508—549).

—This paper is a critical examination of experiments by Seegen and Novak, by which they endeavoured to show that nitrogen in the gaseous state was eliminated from the body by the skin and lungs.

The authors first object to the gas-holder used by Seegen and Novak, which was immersed in oil, on the ground that diffusion was possible between the contents of the gas-holder and the external air through the oil. This they demonstrated to be the case by a series of experiments.

Their second objection is to the method of preparing oxygen used



by Seegen and Novak from black oxide of manganese and potassic chlorate, the resulting oxygen being well known to be impure.

It is also urged that the ammonia evolved from the excreta of the animals experimented upon is an obvious source of the nitrogen found in the expired air. Seegen and Novak in their account of their experiments remark that the animals could not be kept very long in the respiration apparatus without exhibiting symptoms of distress. This the authors regard as further confirmation of their theory that they were supplied with impure air. They quote experiments to show that a mixture of manganese dioxide and potassic chlorate evolves chlorine.

The temperature in Seegen and Novak's chamber was taken by one thermometer only. The authors have made large numbers of experiments with similar apparatus, and find several thermometers necessary, variations amounting to 3—4° C. being often recorded in different parts of the same chamber. On these grounds they are of opinion that Seegen and Novak's statement that gaseous nitrogen is evolved from the skin and lungs must be accepted with great reservation.

W. N.

**Absorption in the Stomach.** By H. TAPPEINER (*Zeitschr. f. Biol.*, 16, 497—508).—The author's method of experiment was to ligature the pyloric end of the stomach in dogs and cats, and then inject known quantities of readily determinable substances. In a dog, 3·5 hours after the injection of 1·73 gram grape-sugar, 1·63 gram was recovered. Of 0·568 gram sodium sulphate, 0·477 gram was recovered after the same lapse of time. In another experiment on a cat, 1·28 gram grape-sugar was injected, and 1·25 gram recovered after three hours; of 0·670 gram tannin, 0·594 gram was recovered; of 10·7 grams peptone, 9·6 grams were found to be unabsorbed. Strychnine given under the same conditions was found to require a very long time to develop its effect.

The above were all given in watery solution. The results were entirely different when an alcoholic solution was used. A cat weighing 2 kilos. took 0·04 gram strychnine dissolved in 5 c.c. 90 per cent. alcohol, and 15 c.c. water, and died in 10 minutes, whilst a smaller animal took 0·1 gram strychnine dissolved in 70 c.c. water, and survived three hours.

With a view to determine whether the ligature had any influence in bringing about these results, another method was adopted. Through an artificial gastric fistula a small rubber bag was introduced into the pylorus, and the aperture closed by distending the bag with air. Various difficulties had to be encountered, not the least of which was persistent vomiting, which prevented the trial of some of the previous substances.

Chloral hydrate was therefore tried; 6·5 grams produced deep narcosis in 10 minutes with the pylorus open; the same quantity in watery solution, with the pylorus ligatured, produced little or no effect. Alcoholic solution of chloral acted nearly as quickly (although the results were not so constant) with the pylorus ligatured as when open. During the chloral narcosis, the experiment with grape-sugar was

repeated, a watery solution was practically not absorbed, and very little of an alcoholic solution: with alcohol alone, above two-thirds was absorbed.

W. N.

**Action of Diastatic Ferments on Starch, Dextrin and Maltose.** By v. MERING (*Zeitschr. f. Physiol. Chem.*, 5, 185—197).—The author thus summarises his results:—

(1.) Starch when acted on by saliva or diastase yields dextrin and maltose at first, but by prolonged action some grape-sugar is produced as the result of decomposition of the maltose.

(2.) Maltose after the action either of large quantities of diastase or of saliva for a short time (2 hours), is not sensibly altered; by longer action, grape-sugar is formed. On the other hand, grape-sugar is not produced either by the fermentation or putrefaction of maltose.

(3.) By the action of saliva or diastase on amyllum, two different dextrins are produced, of which one is attacked by ferments, the other not. The former yields maltose at first, and later grape-sugar. Another dextrin was found to be attacked by saliva and not by diastase.

W. N.

**Tissue Change on a Milk Diet.** By CAMERER (*Zeitschr. f. Biol.*, 16, 493—507).—The experiments were made on two girls aged respectively 12 and 10 years, whose diet for a period of four days consisted only of milk and a little coffee. The experiments could not be further prolonged on account of the rejection of the diet. The results were as follows: No. 1 took daily 1915 grams milk, containing 10.59 grams nitrogen, 53.7 grams fat, and 91.3 grams milk-sugar. There were excreted by the urine 8.86 grams nitrogen; in the fæces, 0.58 gram nitrogen, and 1.5 gram fat, showing a deficit of 1.15 gram nitrogen.

No. 2 took daily 1914 grams milk, containing 11.3 grams nitrogen, 57.4 grams fat, 97.6 grams milk-sugar: 8.81 grams nitrogen were excreted in the urine, and 0.38 in the fæces, the proportion of inorganic salts taken in and excreted were also carefully estimated.

W. N.

**Consumption of Tissue in Starving Herbivora.** By M. RUBNER (*Zeitschr. f. Biol.*, 17, 71—77).—(1.) *The albuminoids.* (a.) The quantity of nitrogen excreted. The investigations were made on rabbits. The urine was collected in cages in the usual way. The animal sat on a wide-meshed sieve of wire, through which the fæces dropped on to a second sieve, the meshes of which were fine enough to retain them. The nitrogen was estimated in the urine only, since, according to the author's experience, the quantity in the fæces of a starving animal is quite insignificant. The most important cases were Nos. II, III, and V, the animals living 9, 19, and 19 days respectively. The following table exhibits the results as far as nitrogen was concerned:—

	Day.	Total nitrogen.	Mean nitrogen per diem.	Mean proteid exchange per diem.
Rabbit II .. {	1—3	5.03	1.67	10.86
	4—5	2.92	1.46	9.49
	6—8	9.65	3.21	20.87
Rabbit III .. {	1—2	3.00	1.50	9.75
	3—8	6.18	1.03	6.70
	9—15	6.34	0.91	5.92
	16—18	7.94	2.65	17.23
Rabbit V.... {	1—7	4.495	0.642	4.17
	8—13	4.803	0.646	4.46
	15—18	5.662	1.415	9.20

Similar results have been obtained in carnivores. The proteid exchange is considerable at first, then diminishes greatly, and is again enormously increased just before death.

(b.) After death, the amount of nitrogen in the whole animal was investigated, and the nitrogen of the urine being known, the total nitrogen in the animal at different periods could be estimated. The nitrogen eliminated by the urine in the first period of the starvation amounted to 2 to 3 per cent. of the total nitrogen in the animal's body, in the later periods to 7.35—7.73 per cent. of the whole. Voit only found 0.8 per cent. in a dog weighing 35 kilos.

The daily nitrogen excretion per 1 kilo. of body weight was very much the same as in a dog of the same weight, namely, 0.51 gram to 0.57 gram as against 0.53 gram in the dog; for a heavier dog of 33 kilos. only 0.18 gram was excreted, and in an ox only 0.08.

(2.) *The fat exchange* was determined as follows:—

By means of Voit's small respiration apparatus, the CO<sub>2</sub> elimination was observed. The carbon in the urine was also determined, and from the sum of these two factors the total daily elimination of carbon was calculated. The decomposition of proteids was calculated from the nitrogen excreted; the amount of carbon to be accounted for in this way was calculated and subtracted from the total. The remainder was reckoned as fat, with the following result:—

Rabbit II per diem, on the second day, 10.3 grams; on the fourth, 10.3 grams; on the eighth, 2.4 grams. Rabbit III, third to eighth day per diem, 10.0 grams, ninth to fifteenth day, 7.4 grams; sixteenth to nineteenth day, 1.0 gram per diem, thus showing that at the end of the experiment, when the store of fat failed, there was a large compensatory destruction of proteid: the ratio was calculated to be 100 parts proteid for every 43.31 parts fat. These figures agree very fairly with Henneberg's 100 to 41.5.

W. N.

**Influence of Sodium and Calcium Carbonates on the Proteid Metabolism of the Body.** By A. OTT (*Zeitschr. f. Biol.*, 17, 165—183).—The author's investigations were made on a dog weighing 10 kilos., and which was maintained in nitrogenous equilibrium on a diet of 500 grams meat daily. The nitrogen of the meat was estimated

by combustion with soda-lime, the urea by titration with mercuric nitrate.

The investigations of the properties of sodium carbonate were made in three successive periods of 10, 7, and 11 days respectively. In the second period, the dog took daily 2 grams sodium carbonate (the amount of water in the salt is not mentioned) with the following results:—

Nitrogen.	Period I.	Period II.	Period III.
Ingested .....	168·20	116·55	179·00
Excreted .....	162·57	112·80	173·32
Deficit .....	— 5·625	— 3·74	— 4·67
Corrected deficit ..	— 1·148	— 0·64	— 0·13

from which the author concludes that the sodium carbonate exerted no influence on the proteid metabolism. The action of calcium carbonate was investigated in a precisely similar manner; the second period was of eight days' duration, on six of which the animal took 5 grams, and on the last two 10 grams calcium carbonate. The body weight was very constant; in this experiment, the reaction of the urine was nearly always neutral, only twice alkaline.

Nitrogen.	Period I.	Period II.	Period III.
Ingesta .....	128·76	135·25	102·10
Excreta .....	130·64	128·76	100·94
Difference (not corrected) .....	+ 1·87	— 6·49	— 1·16

These differences were considered too slight to base any conclusions upon them. The elimination of lime salts was not investigated.

W. N.

### Importance of Light for the Formation of Hæmoglobin.

By G. TISSONI and M. FILETI (*Bied. Centr.*, 1882, 210).—The amount of hæmoglobin in the blood of animals kept in the dark decreases, whereas the opposite occurs if they be fully exposed to light.

E. W. P.

**Variations in the Composition of the Serum after Blood-letting.** By G. BIZZOZERO and C. SANGUIGIO (*R. Accad. delle Scienze di Torino*, 16, 71—75; *Gazzetta*, 1881, 540). The experiments were made on dogs, which, in the first series, were allowed to eat freely after blood-letting; and it was then found that, while the proportions of the inorganic constituents of the serum remained constant, the organic solids diminished suddenly, and continued to diminish for several hours, after which time they began to increase, and continued to do so till, after 14 days, they exceeded the normal quantity. When, on the other hand, the dog was kept without food, it was found, contrary to all expectation, that the solid substances of the serum, which had diminished immediately after the blood-letting, began to increase sooner than in the former case, so as to exceed the normal amount after two days. In this experiment, it was noticed that when food was given to the animal, the proportion of solids in the serum imme-

diately diminished. In other experiments, it was found that the mere state of fasting gave rise to a perceptible increase in the proportion of solids in the serum.

H. W.

### **Soluble and Insoluble Modifications of the Gastric Ferment.**

By A. GAUTIER (*Compt. rend.*, **94**, 652—655).—Solution of pepsin from the sheep, filtered twice through paper, and then through biscuit porcelain, still retains the property of rapidly dissolving fibrin, and converting it completely into peptone. It has, however, only about half the digestive power of the unfiltered liquid. This soluble pepsin has also the property of fixing itself on fibrin in an insoluble form, as recently observed by Wurtz (this vol., p. 536). The portion left on the filter, after prolonged washing, consists mainly of rounded or ovoid refractive corpuscles, about one-tenth or one-twelfth the diameter of the globules of beer yeast. They have a somewhat slow, non-brownian motion, and are frequently associated in pairs, in which condition they appear to be more mobile. They are accompanied by numerous agglomerations of brilliant immobile corpuscles, together with crystals of ammonium magnesium phosphate, fatty globules, and here and there very small bacteria: 0.086 gram of the dry insoluble matter was obtained from 4 grams of pepsin. This insoluble portion, in presence of dilute hydrochloric acid, has a power of dissolving fibrin six times greater than that of the unfiltered pepsin, but the process of digestion is not complete, even after a long time, the fibrin being converted into intermediate products, which are precipitated by nitric acid. The insoluble particles are probably protoplasmic granules from the peptogenic cells. In presence of pure water, they are slowly converted into soluble pepsin. Their action is not affected by considerable quantities of hydrocyanic acid.

C. H. B.

**Microzymes of the Gastric Juice.** By BÉCHAMP (*Compt. rend.*, **94**, 582—585).—The *microzymes* were isolated from the gastric juice by filtering and then treating the residue on the filter with ether, in order to remove fat. Under the microscope, they appear as brilliant granules, somewhat larger than the pancreatic microzymas. After washing with a very dilute solution of phenol, they do not redden litmus. 0.6 gram of the microzymes convert 50 grams of starch into the soluble modification in 24 hours at 40°, without formation of either glucose or dextrin. If the action is allowed to go on longer, the mixture becomes acid. Under the same circumstances pancreatic microzymes convert starch into sugar. Gastric microzymes are without action on a solution of sugar containing creasote, neither have they any action on fibrin or casein in pure water, but if the liquid is acidified with hydrochloric acid to the same extent as gastric juice, the fibrin and casein are rapidly dissolved. The gastric juice of the dog does not entirely dissolve casein, but leaves an insoluble residue. Primovalbumin is not attacked by the microzymes in pure water, but in presence of hydrochloric acid it is rapidly dissolved, being converted into two substances, one soluble in alcohol, the other insoluble. Probably pepsin is formed by the gastric microzymes, just as pancreazymase is formed by the pancreatic microzymes. The action of the gastric

microzymes never gives rise to the formation of crystalline bodies, such as leucine, tyrosine, &c. C. H. B.

**Gastric Digestion.** By E. DUCLAUX (*Compt. rend.*, 94, 736—739).—The author has found that amongst the ferments of casein is a diastase capable of converting it completely into peptone. The stomachs of animals contain a large number of different ferments, and the majority of these secrete diastases. The diastases of sugar and starch are sometimes present in, sometimes absent from, the gastric juice in the stomach of the sheep and dog, and are always absent from the gastric juice extracted from the glands. It follows that the digestion of starchy matter either does not take place in the stomach, or, if it does, is due to the action of ferments. Boiled starch may be kept for more than a year in pure gastric juice without losing its power of giving a blue colour with iodine. The diastases of albuminoid matters are rarely present in the stomach, and the digestion of such matters is left mainly to the gastric juice. The latter attacks different albuminoids with different degrees of facility. It coagulates casein, but does not alter the coagulum formed: hence neither in the young nor in the adult is milk digested by the action of the juice secreted by the mucous membrane. Raw albumin offers considerable resistance to the action of the gastric juice, but cooked albumin is more readily attacked, so are gluten and blood fibrin. In consequence of this unequal action of the gastric juice, different parts of muscular fibre are differently acted on. The same unequal action serves to explain the fact that the juice does not attack the cells in which it is secreted.

C. H. B.

**The Pancreatic Secretion of Man.** By E. HERTER (*Zeitschr. f. Physiol. Chem.*, 4, 160—164).—The first case investigated by the author was one in which a tumour pressed upon the end of the pancreatic duct, so that the pressure of the secretion dilated it considerably. A quantity of fluid, about 2 grams, was obtained; this was almost clear, slightly yellow in colour, strongly alkaline in reaction, and acted powerfully on starch, proteids, and fats. It contained peptone, but no albuminoids or sugar. The ash was rich in alkaline phosphates; the solid residue amounted to 24.1 per 1000, of which 17.9 was organic matter, and 6.2 ash; of the organic matter, 11.5 consisted of peptone and ferment (insoluble in alcohol), and 6.4 was soluble in alcohol.

The author further examined two cases of pancreatic cyst with atrophy of the gland substance. No. I yielded 24.1 parts per 1000 dry residue, of which 14.9 was organic matter, 9.2 ash. No. II had almost exactly the same composition. Both contained only diastatic ferment; neither fluid had any action on fibrin or fat. W. N.

**Researches on the Pancreatic Secretion.** By E. HERTER and others (*Bied. Centr.*, 1882, 183).—Herter found that the fluid contained in a pancreatic cyst consisted of 24.1 parts per 1000 of solid matter, of which 14.9 were organic, and the rest mineral. The fluid behaved as a diastatic ferment, not acting on fat and fibrin. Brown and Heron found that the aqueous extract of the pancreas acts at 40° on starch in the same

manner as diastase at 60°; pancreas diastase, like malt diastase, converts achroodextrin into maltose, and at 40° changes maltose slowly into dextrose; this property is not possessed by malt extract; there is no ferment present which inverts cane-sugar; intestinal fluid inverts cane-sugar, changes maltose into dextrose, but only acts feebly on starch. Béchamp obtains *microzymin* by treating the pancreas first with water, and then with alcoholic ether and water; this substance converts starch rapidly into grape-sugar, and dissolves albumin; its action is analogous to that of yeast-cells on cane-sugar. E. W. P.

**Gases of the Bile.** By J. CHARLES (*Pflüger's Archiv.*, 26, 201—218).—In these experiments, the bile was collected by means of a cannula tied into the *ductus communis choledochus*, which by means of a caoutchouc tube was connected with a Geissler's pump, so arranged that the air in the connecting tube could be removed, and phosphoric acid introduced to expel the carbonic anhydride, which it was the chief object of the author to estimate. The oxygen and nitrogen were estimated together in three experiments upon rabbits, the free carbonic anhydride was found to be between 9·75 and 16·94 volumes per cent.; the combined carbonic anhydride between 90·82 and 105·18 volumes per cent.; the total was on an average 109·5 per cent. Two experiments on dogs gave free carbonic anhydride, 17·1 and 14·28 volumes per cent. respectively; combined carbonic anhydride, 29·45 and 141·96 vols. per cent.; total carbonic anhydride, 46·55 and 57·24 per cent. A third experiment on one of the same dogs gave 100·15 vols. per cent. All the figures were obtained at a pressure of 1 meter of mercury. The carbonic anhydride in the bile seems without doubt to exist as alkaline carbonates, and the quantities in herbivores to be very considerable, probably on account of the nature of their food. W. N.

**Composition of Mixed Human Saliva.** By F. HAMMERBACHER (*Zeitschr. f. Physiol. Chem.*, 5, 302—308).—In 1000 parts mixed saliva from a healthy young man the author found—

Water .....	994·203
Solids .....	5·797
Epithelium and mucin .....	2·202
Ptyalin and albumin .....	1·399
Inorganic salts .....	2·205
Potassium sulphocyanate .....	0·041

In 100 parts of the solids were 37·985 parts epithelium and mucin, 23·978 ptyalin and albumin, 38·037 inorganic salts. The ash contained—

K.	Na.	CaO.	MgO.	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	Cl.
45·71	9·59	5·01	0·16	18·85	6·38	18·35

1·803 per cent. of the sulphuric acid existed as such; the rest is derived from the organic matter. W. N.

**On Urea in the Liver.** By HOPPE-SEYLER (*Zeitschr. f. Physiol. Chem.*, 5, 348).—The author found in the liver of a recently killed dog

a base, soluble in alcohol, but no urea, or at the most the merest traces. He failed to find either leucine or tyrosine in the blood or liver.

W. N.

**Influence of Muscular Work on the Elimination of Sugar and Urea in Diabetes.** By H. OPPENHEIM (*Pflüger's Archiv.*, **26**, 259—263).—The investigations were made in a severe case of diabetes, the patient passing on an average more than 200 grams of sugar daily. The work consisted in pumping water, and was so arranged that several days of rest intervened between any two days on which work was done. The amount and nature of the work was so regulated as not to cause dyspnoea. The author found that although the urea elimination in the period of rest, despite a regulated diet, was not constant, there was an undoubted increase on the working days, *e.g.*, in the first rest period the mean daily elimination was 50 grams, on the day of work 59.4 grams, and on the day following 66.6 grams. There was no satisfactory evidence that the work affected the sugar elimination.

W. N.

**Acid Fermentation of the Urine.** By F. RÖHMANN (*Zeitschr. f. Physiol. Chem.*, **5**, 94—121).—The author found, contrary to Scherer, that an increase of the acids in urine when exposed for some time to air, occurred only in exceptional cases, and that then, in all probability, it depended on the presence in the urine of sugar, alcohol, or other bodies which yield acids by fermentation. As a rule, the acidity and amount of ammonium salt remained unchanged at first; but as the ammonium increased, the acidity fell, and finally the reaction became alkaline. Whilst the urine has an acid reaction, it is proportionately cloudy, and contains an appreciable amount of nitrous acid, the presence of which can be demonstrated by adding a little sulphuric acid and iodide of potassium paste. Schöenbein has already determined the fact that fresh urine contains nitric acid (probably arising from drinking water or the vegetable used as food), and the author has been able to obtain nitric oxide from urine. Whether the nitrous acid exists as such preformed in the urine, or whether it is a product of the decomposition of the nitric acid known to be present, the author was unable to determine, since small traces of nitrous acid cannot be detected in urine by the iodine reaction. The reduction is easily conceivable in the presence of a fungus; possibly also it results directly from the oxidation of ammonia. The nitrous acid diminishes by degrees as the urine becomes alkaline.

W. N.

**Bodies in Urine Precipitable by Phosphotungstic Acid.** By T. HOFMEISTER (*Zeitschr. f. Physiol. Chem.*, **5**, 67—78).—The author has already used this reagent for the detection of peptone in urine, and has now applied it to urines not containing peptone. 10 litres of dog's urine, after a meat diet, were treated with 1 litre of hydrochloric acid and then with phosphotungstic acid, so long as any precipitate was produced. This precipitate was then washed with dilute sulphuric acid (1 in 20 by vol.) until the chlorine reaction disappeared. After treating further with baryta-water, the precipitate contained kynuric acid and kreatinine, but no xanthic bodies. Human urine treated in the same way yielded no kynuric acid, but kreatinine and



xanthine (hypoxanthine?). From these experiments, it follows that the compound of kynuric acid, kreatinine, and xanthine, with phosphotungstic acid, must be very insoluble in water. Direct experiments confirm this. A solution of kynuric acid in baryta-water containing only 1 part in 4000 became cloudy at once on addition of hydrochloric acid and phosphotungstic acid, and soon deposited a precipitate of rhombic tables; even in solutions containing only 1 part in 16,000 this occurred after 24 hours' standing. A solution of kreatinine, containing 1 part in 12,000, was also precipitated after 24 hours. The peptone reaction is not prejudiced by the presence of kreatinine; kreatinine is not precipitated in acetic acid solution by the reagent, whilst peptone is precipitated. When urine is suspected to contain peptone, the last traces of albumin are removed by lead acetate, then treated with one-fifth vol. acetic acid, and finally with a solution of sodium phosphotungstate, made acid with acetic acid; any cloudiness or precipitate indicates peptone. W. N.

### **Oxidation of Aromatic Substances in the Animal Body.**

By C. PREUSSE (*Zeitschr. f. Physiol. Chem.*, **5**, 57—66).—The author investigated the behaviour of the three isomeric cresols when taken into the alimentary tract, with the following results:—(1.) Paracresol gave parahydroxybenzoic acid; the major part was however excreted unchanged in the form of the cresyl-hydrogen sulphate. (2.) Orthocresol, by analogous oxidation, should yield salicylic acid. This was however clearly proved not to be present in the urine. On the other hand, the ethereal extract of the urine, after treatment with hydrochloric acid, yielded a body having the properties of quinol. The analysis gave values closely approximating to those of toluquinol. The major part again was discharged as the cresyl hydrogen sulphate. (3.) Metacresol should yield metahydroxybenzoic acid; this was certainly not detected, and the bulk of the metacresol was excreted as before. Further experiments were made with parabromotoluene and orthobromotoluene. The former was oxidised like toluene, and yielded parabromobenzoic acid, which was in great part converted into parabromhippuric acid. There was no formation of the sulphate. No bromine was found in the urine, as such. Very similar results followed the use of orthobromotoluene, orthobromhippuric acid being found in the urine, but no free bromine. W. N.

**Synthetic Processes in the Animal Body.** By E. BAUMANN and C. PREUSSE (*Zeitschr. f. Physiol. Chem.*, **5**, 309—343).—After feeding dogs for some months with bromobenzene in quantities of from 3 to 5 grams per diem, the authors found in the urine two groups of bodies:—(1.) Compounds in which the bromobenzene residue,  $C_6H_4Br$ , was combined with organic bodies containing sulphur and nitrogen. The latter are intermediate products of tissue change, which by their union with bromobenzene were protected from further change. (2.) Oxidation-products of benzene, mon- and di-atomic phenols which passed into the urine as etheric hydrogen sulphates. The urine directly after being passed generally exhibited a strongly marked laevorotary action, and reduced alkaline solutions of cupric hydroxide

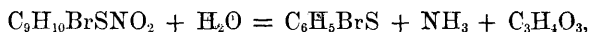
on boiling. These properties disappeared when the urine was strongly acidified, and simultaneously a considerable separation of an acid occurred.

*Bromophenylmercapturic acid*, a product of the decomposition of the lævorotary substance, may be prepared by treating the urine with one-twelfth of its volume of lead acetate solution, filtering, and adding one-tenth of its volume of strong hydrochloric acid, and after eight to ten days filtering again. The precipitate is twice recrystallised from hot water, dissolved in alcohol, and again poured into boiling water. On cooling, the acid separates out in needle-shaped crystals an inch long. The formula given by the authors agrees with that found by Jaffe, viz.,  $C_{11}H_{12}BrSNO_3$ ; it is soluble in 70 parts of boiling water, almost insoluble in cold water and ether, somewhat readily soluble in alcohol, is monobasic, and yields readily crystallisable salts, of which the authors describe those of ammonium, barium, and magnesium.

By boiling bromophenylmercapturic acid with 20 or 30 volumes of dilute sulphuric acid for half to three-quarters of an hour with a reflux condenser, the acid takes up 1 mol.  $H_2O$ , and is converted into acetic acid and *bromophenylcystine*,  $C_9H_{10}BrSNO_2$ , i.e., cystine in which 1 atom of hydrogen is replaced by the monatomic group,  $C_6H_4Br$ ; the amount of each of the products of decomposition came very near the theoretical quantity. Bromophenylcystine (m. p. 180—182° C.) forms slender glittering needles and plates, having a greasy feel in the dry state; it is practically insoluble in water, alcohol, and ether. With acids, it forms compounds which crystallise well. The solution in concentrated sulphuric acid is coloured blue on heating, like bromophenylmercapturic acid itself; the coloration disappears on adding water or alcohol. Bromophenylcystine is readily soluble in fixed alkalis and ammonia; with cupric sulphate the ammoniacal solution gives a clear blue crystalline precipitate having the composition  $(C_9H_7BrSNO_2)_2Cu$ . On heating bromophenylcystine with alkalis, it is broken up into bromophenylmercaptan and ammonia. Phenylmercapturic acid undergoes the same decomposition, except that acetic acid is also formed. Besides these products, there is formed in both cases an acid which the authors have not yet been able to isolate in a pure state, but which, from its decomposition-products and reactions, viz., oxalic and uvitic acid, appears to be pyruvic acid. The whole of the nitrogen of the bromophenylcystine is converted into ammonia. In order to separate the bromophenylmercaptan, the solution is acidified with dilute sulphuric acid, boiled for half an hour and then distilled; the mercaptan comes over entirely in the early part of the distillation with water, partly as crystals, and partly as an oil which on cooling solidifies to a crystalline mass (m. p. 74—75°; b. p. 230°). It is almost insoluble in cold water, slightly soluble in hot, and readily in alcohol, ether or chloroform. With mercuric chloride, the alcoholic solution gives a white precipitate; with cupric chloride, a yellow flocculent precipitate, which is also obtained when bromophenylcystine or the mercapturic acid is treated with Fehling's solution. On warming bromophenylmercaptan with concentrated sulphuric acid, it exhibits the reaction which, according to the authors, is characteristic of the aromatic sulphides and sulphy-

drates in which the sulphur is combined with the carbonic anhydride of the aromatic radicle. The pyruvic acid, according to the researches of Wislicenus and Debus, is readily converted by nascent hydrogen into fermentative lactic acid. For the preparation of large quantities of the latter, the authors use bromophenylcystine, which is dissolved in soda and treated with sodium-amalgam on the water-bath, until the evolution of ammonia ceases. After separation of the phenylmercaptan by agitation with ether, the acid may be separated; it was identified by the analysis of its calcium and zinc salts.

*Constitution of Bromophenylcystine and of Cystine.*—The decomposition of bromophenylcystine into bromophenylmercaptan, ammonia, and pyruvic acid, which takes place according to the equation—



shows that bromophenylcystine is a derivative of pyruvic acid, with which the aromatic residue,  $\text{C}_6\text{H}_5\text{Br}$ , is combined through the sulphur. The rational formula of bromophenylcystine, according to the authors, is  $\text{COOH.CMe}(\text{NH}_2).\text{S.C}_6\text{H}_5\text{Br}$ , and of cystine itself,—



According to this formula, the decomposition of cystine by alkalis must result in the formation of pyruvic acid, hydrogen sulphide, and ammonia. Dewar and Gamgee have already shown that pyruvic acid is probably one of the products of the decomposition of cystine, although this is not absolutely certain. The formula of cystine would thus be, not  $\text{C}_3\text{H}_5\text{NSO}_2$ , as the authors write it, but  $\text{C}_3\text{H}_7\text{NSO}_2$ , in accordance with the latest analyses by Hoppe-Seyler. By the action of acetic anhydride, the authors obtained from mercapturic acid as well as from bromophenylcystine, a neutral body, apparently an anhydride, which they name bromophenylcystine.

By treating bromophenylmercapturic acid with sodium-amalgam, the bromine is by degrees separated from the molecule and phenyl mercapturic acid is formed, which by decomposition with acid yields phenylcystine. Out of 100 grams of bromobenzene given with the food, the authors obtained 20—30 grams. As such it was obtained also from the urine of rabbits, but only in small quantities.

Amongst the products formed from bromophenol and the animal body are, bromophenol, already described by Steinauer—bromoquinol, and bromocatechol. W. N.

**On Human Milk.** By P. RADENHAUSEN (*Zeitschr. f. Physiol. Chem.*, 5, 13—30).—According to the author, human milk behaves differently from cow's milk when shaken with ether, in that it loses its opacity, whilst cow's milk requires the previous addition of caustic soda in order to bring about this result. For the preparation of the albuminoids, the milk was carefully neutralised with very dilute sulphuric acid, and precipitated with 1 to 2 volumes of alcohol. The precipitate was first treated with 50 per cent. alcohol, then with strong alcohol, and finally the fat was removed by ether. From the behaviour of this precipitate with reagents, the author concludes that

it is not true casein but an albumin. Traces of peptone were found in the alcoholic washings. W. N.

**On Milk.** By L. HERMANN (*Pflüger's Archiv.*, **26**, 442—444).—Zaber, from the fact that by filtering milk under diminished pressure through porous porcelain, a clear filtrate, free from casein, was obtained, concluded that the casein was not really in solution in the milk. The author conjecturing that possibly the porcelain surface played some specific part, tried the effect of adding finely pulverised porcelain to milk in the proportion of four of the former to three of the latter, and obtained a perfectly clear fluid, which yielded no precipitate with acetic acid. If less powder were added, the filtrate was cloudy and gave a precipitate with acetic acid, although this was only slight and readily soluble in excess. Animal charcoal behaved towards milk in precisely the same way as powdered porcelain: the longer the mixture stood the less was the amount of the precipitate obtained by adding acetic acid. W. N.

**Certain Constituents of Pus from the Human Subject.** By L. BRIEGER (*Zeitschr. f. Physiol. Chem.*, **5**, 366—369).—The author found in fresh stinking pleuritic exudata, which contained relatively large quantities of phenol, an acid which he believed to be similar to the parahydroxyphenylacetic acid found by E. and H. Salkowski in decomposing albumin. In 750 c.c. of another similar fluid, the author detected succinic acid and another acid whose melting point was 98°, which appeared to him to be glutaric acid. W. N.

**Origin of Hypoxanthine in the Organism.** By A. KOSSEL (*Zeitschr. f. Physiol. Chem.*, **5**, 152—157).—Nuclein, prepared from pus cells and containing 3·2 per cent. of phosphorus and 1·6 per cent. sulphur, yielded by prolonged boiling 1·03 per cent. hypoxanthine, and thereby 80·3 per cent. of the phosphorus present was converted into phosphoric acid. Larger quantities of nuclein were prepared from goose's blood, by dissolving the corpuscles in water and ether, washing the residue with water, purifying by digestion and boiling with alcohol. Three separate preparations obtained in this way were found to contain 6·04 per cent., 6·49 per cent., and 7·12 per cent. phosphorus respectively. When mixed and submitted to prolonged boiling, they yielded 2·64 per cent. hypoxanthine. W. N.

**Physiological and Pathological Chemistry of the Eye.** By A. CAHOUS (*Zeitschr. f. Physiol. Chem.*, **5**, 214).—*The Retina.*—The retinae of oxen, pigs, and horses, were examined as fresh as possible, and were found to have a distinctly alkaline reaction. The following composition was found for the retina of the ox:—Water, 86·52; albuminoids, 6·77; bodies resembling albuminoids, 1·59; alcohol extract, 0·25; watery extract, 0·52; cholesterin, 0·77; fat, 0·47; lecithin, 2·08; soluble salts, 0·93; insoluble salts, 0·02; cerebrin, traces; in the ash sodium chloride and phosphate preponderated. Details of other analyses are also given. The lecithin, cholesterin, and cerebrin appear to be present in the retina in much the same

proportions as in the grey matter of the brain. Cholesterin and cerebrin appear also to be constituents of the axis cylinder of medullated nerve-fibre. The albuminoids appear to be very complicated, and could not with any certainty be separated—myosin, serum-albumin, and a body resembling mucin. Besides these, other bodies "resembling" albuminoids were obtained by heating retinæ in various solvents at 120°: the author thinks he found tunicin, and a body resembling Schmidt's propepton (Kühne's hemialbumose). The ether extract of the retina was blackened by osmic acid, and contained lecithin, but no cholesterin or cerebrin. The author does not state his reasons for believing the blackening by osmic acid to be due to lecithin, and not to fat, of which this is a characteristic histological reaction. The vitreous and aqueous humours were found to have a very similar composition.

	<i>Humor vitreus.</i>	<i>Humor aqueus.</i>
Albumin .....	0.074	0.082
Other organic matter ..	0.071	0.148
Ash.....	0.971	0.993
Water.....	98.884	98.770

The author also made some analyses of eyes affected with cataract, the results of which are given. W. N.

**Action of Urea and Ammonium Salts on Animals.** By C. RICHET and R. MONTARD-MARTIN. (*Bied. Centr.*, 1882, 210.)—One-eighth only of the urea injected into the blood can be detected after half an hour, even if both kidneys are ligatured. The separation of urea by the kidneys is but slow; after 17 hours only 15 grams appeared out of 50 injected. Introduction of urea increases diuresis, so that the percentage of urine to urea falls. After injection of moderate amounts of urea, the animal dies quicker when both ureters are ligatured than if the kidneys had been excised. Considerable quantities of ammonium chloride can be safely injected under the skin. The mucous membrane of the stomach of animals which die of uræmia is strongly ammoniacal. E. W. P.

**Adipocere.** By J. KRATTER (*Zeitschr. f. Biol.*, 16, 455—491).—The author studied the formation of adipocere in human extremities, which were macerated in glass vessels filled with water. The formation began in the subcutaneous fat and in the marrow of the bones, later in the skin, and still later (never earlier than three months) in the muscles. By microscopic examination, he was able to watch the process of transformation in the muscles. W. N.

## Chemistry of Vegetable Physiology and Agriculture.

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**Development of Yeast in Solutions containing a Varying Quantity of Nitrogen.** By M. HAYDUCK (*Bied. Centr.*, 1882, 208).—A solution of 50 grams acid potassium phosphate and 17 grams magnesium sulphate dissolved in a litre of water was employed, and 20 c.c. of this solution was mixed with a 10 per cent. sugar solution and varying amounts of asparagine, the whole being made up to 1 litre; in each case, 2.5 starch free from yeast was employed. The results obtained were, the nitrogenous matter was only assimilated up to a certain degree of concentration; a separation of nitrogen by the yeast was in all cases observed; in dilute solutions, the yeast always contained a constant minimum amount of nitrogen, whilst the quantity of yeast remained proportional to the quantity of nitrogen; in solutions containing more nitrogen, the quantity of yeast remained constant, but the amount of nitrogen combined with the yeast increased proportionally to the nitrogen in solution. When, however, the nitrogen was increased to a still greater degree, no effect on the yeast was noticed. Generally the activity of the yeast is accompanied by an increase in its amount of nitrogen. Yeast can propagate itself in a pure sugar solution (ash being present), but a portion of the nitrogen in the principal cells is employed in the formation of the new ones. The growth of yeast is influenced by the amount of alcohol formed, this substance being detrimental to its growth. E. W. P.

**Growth of Starch Grains by Intussusception.** By C. NÆGELI (*Bied. Centr.*, 1882, 186—190).—A critical paper in which Naegeli denies the correctness of Schimper's theory of intussusception (*Abstr.*, 1882, 1061). E. W. P.

**Certain Bye-products of Plant Development.** By H. DE VRIES (*Bied. Centr.*, 1882, 191—194).—Those substances which are produced in many plants, but play no apparent part in the formation of its structure, have been termed bye-products; amongst these substances are placed such matters as resin, caoutchouc, &c. The object for which these bye-products are formed is to act as a salve or dressing for such portions of the plant as may be wounded at any time, and this object is the more apparent when such trees as firs are compared with those producing leaves, and in which a healing fluid is absent, these latter suffering the most severely from any damage done to them. E. W. P.

**Observations on the Composition of Steeped Barley.** By G. HEUT (*Bied. Centr.*, 1882, 203).—Ullik (*Abstr.*, this vol., 645) having investigated the influence of various waters on the composition of barley steeped in them, the author has taken up the other side of the question, viz., the influence of distilled water on the composition of various barleys at a temperature of 15—17°. Bohemian and Bavarian were the two kinds used: their composition is compared with

that of the kind used by Ullik, and it is found that the mineral constituents vary very considerably. By soaking, Bohemian barley loses nearly twice as much potash as Bavarian barley, and phosphoric acid is removed simultaneously with the potash. In Bavarian barley there is more iron, and this may prevent the loss of much phosphoric acid. Bohemian loses less total organic matter, but the same quantity of nitrogen in the form of peptone is withdrawn from both.

E. W. P.

**Composition of American Grasses.** By C. RICHARDSON (*Amer. Chem. J.*, 4, 16—22).—This paper gives the results of analyses of a large number of grasses, made in the laboratory of the Department of Agriculture at Washington, the averages of which are of great interest, both in comparison with those of Wolff for German grasses, and as showing the relations of cultivated and wild grasses to each other, and the variations of composition which one species may present when grown on different soils and in different climates.

*Average Composition of Grasses in Bloom.*

	American.				German.		
	77 analyses of wild grass.	21 analyses of grasses from one farm in Pennsylvania.	10 analyses of grasses from Dept. grounds.	6 varieties of orchard grass from various localities.	Wolff's averages.		
					Fair.	Good.	Very good.
Ash .....	7.90	7.95	7.44	7.38	6.30	7.23	8.24
Fat .....	2.90	3.12	3.52	3.33	2.34	2.92	3.29
Non-nitrogenous extract	53.90	55.75	55.82	55.17	46.53	47.84	48.93
Crude fibre .....	27.10	23.14	22.47	25.19	34.09	30.69	25.77
Nitrogen $\times$ 6.25.....	8.20	10.04	10.25	8.91	10.74	11.32	13.77
Non-albuminous N. p.c.	34.70	30.10	18.30	25.20	—	—	—
Nutritive ratio .....	1:10.2	1:8	1:8	1:9.4	1:7.7	1:7.2	1:5.7

These numbers show that the American grasses differ greatly in composition from German grasses, the proportion of nitrogen in the former being smaller, and that of fibre much smaller; these differences moreover being made up by a larger amount of non-nitrogenous extract and a slight increase of fat. The nutritive ratio therefore varies much more widely than in the German grasses.

The wild varieties of American grass are far inferior in nutritive value to the cultivated, and among the latter, the higher the cultivation the better is the quality, as shown by the averages for the Pennsylvanian grasses, which had not been so highly manured as those from the grounds of the Department of Agriculture in Washington.

Another prominent fact shown by the table is that in the wild grasses the amount of non-albuminoid nitrogen is larger than in the better varieties, and that this amount varies somewhat with the quality of the grass, the more highly cultivated varieties from the grounds of the Agricultural Department having only a little more than half as much as is found in the wild species. The character of the soils may also have had some influence on the results. The wild grasses were for the most part from the sandy soils of the South; those from Pennsylvania grew upon a micaceous loam; and the soil of the grounds of the Agricultural Department is of a heavy nature.

The influence of soil on the proportion of non-albuminoid to albuminoid nitrogen is further shown by analyses, given in the original paper, of *Dactylis glomerata* (orchard or cock's-foot grass), grown on light sandy and on heavy soils, without much cultivation in any case, the result being that the amount of non-albuminoid nitrogen does not increase with an increase in the total nitrogen of the grass, the poorer specimens having more than twice as much relatively to the total nitrogen as the more highly cultivated ones, the diminution of the total amount in the poorer varieties falling largely on the albuminoid forms. The variations in the non-nitrogenous constituents of the plant do not show any regularity dependent on climate or surroundings.

Analyses are also given of meadow fox-tail grass (*Alopecurus pratensis*), showing the changes which take place at various stages of its growth. In this grass, which may be regarded as typical of most cultivated grasses, the total nitrogen diminishes regularly from early to late stages. The albumin diminishes nearly in the same way, but remains constant for a considerable time during the flowering stages.

The non-albuminoid nitrogenous substances, while decreasing rapidly from the first stage at which the grass was collected to nothing at full bloom, increase again slightly after blooming. In many other grasses analysed by the author, this difference is larger and very apparent. Among the non-nitrogenous constituents, the fibre increases towards maturity while the fat decreases. Those substances which make up what is known as the "nitrogen-free extract" in fodder analyses, while they do not present the same regularity of change as the previously mentioned constituents, nevertheless show in a few instances, a regular diminution or increase towards maturity. The sugars, or those substances which are extracted by alcohol and not precipitated by basic lead acetate, and reduce Fehling's solution, do not vary largely, but are more abundant in the young plant than in the other stages, contrary to what was found in the sugar-producing grasses, sorghum and sugar-cane. The organic acids too are present in larger amount in the young plant. A regular diminution takes place in the amount of gum, and a somewhat irregular increase in the indefinite substances extracted by acid and alkali.

The forms of nitrogen which might occur in grasses are ammonia salts, nitrates, albumin, peptones, amides, amido-acids, alkaloïds, and carbamide-bodies. The presence of albumin, ammonia salts, and nitrates, is shown by direct determination. The absence of alkaloids and peptoxes is shown by the non-precipitation of the watery extract



of the plant by phosphotungstic or tannic acid; and the fact that on boiling the aqueous extract of the plant with acids and then distilling with magnesia, no more ammonia is found than before the treatment with acid, points to the absence of amides. Hence it follows that the non-albuminoid nitrogen of the plant must exist in the form of amido-acids. Moreover, these are of different kinds, inasmuch as different reagents do not all act in the same manner in precipitating them: thus there is a substance precipitated by cupric hydroxide, which is not thrown down by tannic acid, or by phosphotungstate; it is probably an amido-acid forming sparingly soluble copper salts. H. W.

**Jacaranda procera**, Sprengel. (*Pharm. J. Trans.* [3], 12, 812.)

—This tree, known in the Brazils as “caroba-carobinha,” “caroba minda,” and “caroba mirim,” grows in the provinces of Rio de Janeiro, Minas, and Espirito Santo. Its leaves and bark were examined by Peckholt in 1866, and his analysis (given below) has lately been confirmed by C. W. Zaremba (*Pharm. Centralhalle*, June 23rd, 1881).

	Leaves.	Bark.
Carobin, crystallised . . . . .	1·620	3·000
Carobic acid, crystallised . . . . .	0·516	—
Steocarobic acid . . . . .	1·000	—
Carobone, balsamic resinous acid . . . . .	26·666	—
Carobaretic acid, inodorous . . . . .	—	2·000
Caroba resin, inodorous, tasteless . . . . .	33·334	5·000
Caroba balsam . . . . .	14·420	—
Bitter principle . . . . .	2·880	2·830
Extractive „ . . . . .	10·550	19·530
Extractive and organic acids . . . . .	10·000	—
Caroba tannin . . . . .	4·390	4·800
Glucose . . . . .	—	1·650
Chlorophyll and wax . . . . .	9·000	—
Calcium malate . . . . .	0·200	76·100
Albumin, starch, dextrin, and salts . . . . .	32·120	
Cellulose and moisture . . . . .	853·304	885·090

Carobin crystallises in silky needles, insoluble in ether, soluble in boiling alcohol and boiling water. It gives precipitates with tartar emetic and ammonium carbonate, the latter precipitate being soluble in excess of the reagent. With acetic acid, it forms a crystalline compound. It is not a glucoside.

Carobic acid forms stellate needles, of aromatic odour and acid taste, soluble in water and dilute alcohol. Lead and copper acetates precipitate carobic acid.

Steocarobic acid is pale-brown, of tonka-like odour, and soluble in cold absolute alcohol and in ether.

Caroborin is greenish, amorphous, and has an aromatic odour; it is soluble in alcohol (sp. gr. 0·815) and in caustic alkalis and alkaline carbonate solutions.

Caroba balsam resembles tonka, having a dark-brown colour and

aromatic odour; it is of a syrupy consistency, and may be evaporated to an almost odourless resin.

Infusions of the caroba leaves are used in the Brazils in place of sarsaparilla in cutaneous affections, and as an antisiphilitic.

L. T. O'S.

### **Wax and Buttery Substance from the Epicarp of the Olive.**

By E. MINGIOLI (*Gazzetta*, 1881, 496—500).—The epicarp of the olive contains about half its weight of a substance, which may be extracted by cold ether, and remains, on distilling off the solvent, in the form of a yellow or faintly reddish-yellow body, which may be purified by digestion with warm alcohol (b. p. 90°), this liquid at 30—40° removing the whole of the colouring matter, and at the boiling heat resolving the substance into two others, one soluble in alcohol of b. p. 90°, the other insoluble and melting at that temperature. The decanted solution, on cooling, deposits a pulverulent waxy substance, whilst the insoluble portion coagulates on cooling to a semifluid jelly.

The *pulverulent waxy substance* is formed of slightly yellowish scales, insoluble in water, soluble in alcohol, very slightly soluble in carbon bisulphide, very easily soluble in ether, chloroform, turpentine-oil, and benzene; tastes like beeswax. It melts at 98—100°, and burns with an odour like that of beeswax, leaving a carbonaceous residue. The quantity obtained was too small for the determination of its specific gravity. Strong sulphuric acid converts it into a reddish mass, changing, after three or four hours, to amethyst, blue and brown. Dilute sulphuric acid dissolves it in the cold, and when heated with it, produces a violet-amethyst coloration, gradually becoming deeper, and changing to blue and ultimately to black. Nitric acid at ordinary temperatures renders it pasty, and at high temperatures colours it first yellow, then brown, and when nearly evaporated sets it on fire. Dilute nitric acid acts less strongly. Strong hydrochloric acid does not alter it further than to cause it to emit an odour of beeswax. It is not attacked chemically by acetic, orthophosphoric, or metaphosphoric acid, but the last two convert it into a glutinous mass. With potash or soda, it forms a glutinous paste, smelling like common soap.

The semifluid buttery substance is less soluble in alcohol than the pulverulent wax, especially in the cold; it quickly becomes resinous on exposure to the air. Dissolves in 300 times its own volume of boiling alcohol. When digested in the cold with alcohol boiling at 90°, it becomes fluid, transparent, and rancid, and presents the appearance of white of egg. It is inodorous when fresh, but emits an odour when rancid. Tastes sweetish in the fresh state, bitter after becoming rancid. It is of a more syrupy consistence than glycerol; stains paper like all fatty substances; solidifies at + 5°. Sp. gr. not exactly determined. It is unctuous to the touch, preserves its fluidity for some time when exposed to the air, but ultimately becomes rancid and more gelatinous, and increases in bulk. It is insoluble in water, very soluble in ether, chloroform, benzene, and turpentine-oil, very sparingly in carbon sulphide. With acids and alkalis, it reacts just like the pulverulent waxy substance.

Bodies very similar to the pulverulent wax have been obtained by

Proust (*Compt. rend.*, **16**, 863) and by Mulder (*ibid.*, **30**, 53) from the epicarp of plums, cherries, and other drupaceous fruits; and the author thinks it probable that all these substances may be identical, the slight differences observed between them being due merely to different degrees of purity. H. W.

**Aconitic Acid in the Scale from Sorghum-sugar Pans.** By H. B. PARSONS (*Amer. Chem. J.*, **4**, 39—42).—Clear defecated sorghum juice, after treatment with milk of lime to faint alkalinity, slowly deposits, on further boiling, a light buff-coloured scale, which adheres tenaciously to the evaporating pan, and, being a poor conductor, causes a considerable loss of available heat. It is mainly an impure calcium salt consisting of 7.95 per cent. water, 24.32 lime, and 67.73 organic matter. On boiling the finely pulverised scale with a quantity of dilute sulphuric acid not sufficient to precipitate all the lime and magnesia present, and mixing the filtrate with twice its volume of absolute alcohol, whereby calcium and magnesium sulphates are precipitated, a second filtrate is obtained which, when evaporated to a small bulk and treated with an excess of absolute alcohol, yields a precipitate consisting of a magnesium salt of the organic acid. An aqueous solution of this salt gave with silver nitrate, lead acetate, &c., the reactions of aconitic acid; and the nature of this acid was further confirmed by quantitative analysis of the zinc, lead, and silver salts prepared from it.

The presence of aconitic acid in molasses from the West Indies was proved by Behr (this Journal, **32**, 182), and its occurrence in the juice of sorghum, a plant somewhat closely related to the sugar-cane, affords another instance of the many similarities in chemical composition which have been noted of late years in plants of the same or closely allied families and orders. H. W.

**Composition of Hay Grown on Hills and Meadows.** By J. R. MOSER (*Bied. Centr.*, 1882, 194).—The upland hay, of which fourteen kinds were examined, was grown at heights varying from 300—1000 m., which ripening later than that grown on the lowland, is richer in albuminoids, and relatively (reckoned on albuminoids) poorer in fibre, consequently it is more valuable as a fodder.

E. W. P.

**Potato Culture.** By NITZKOWSKI and others (*Bied. Centr.*, 1882, 197—201).—Thirty-one kinds of potatoes were grown on a sandy loam previously marled, and manured with liquid manure. The highest yield of tubers was produced by Ceres and Farmers' blush, but Eos produced the greatest amount of starch per acre. Although all kinds were free from disease, yet the percentage of starch per tuber was low. Trophine, 23.16 per cent., being the best. W. Loebe reports concerning the new variety Zborower, that 18 $\frac{3}{4}$  kilos. of "sets" yielded 350 hectolitres per hectare. Schöfauer finds Zborower a more prolific and healthy kind than Biscuit or Zwiebel. Jacobi, out of ten varieties, finds Yellow Rose produces most starch per acre, but that Andersen and Hertha are much more prolific, and resist disease better.

E. W. P.

**Manuring Experiments on Sugar-beet in Brunswick.** By H. SCHULTZE (*Bied. Centr.*, 1882, 163—169).—The questions to be answered were, what influence is exerted on the quantity and quality of the roots by the distance at which they are planted, and also which of the ordinary artificial manures is the best? The seed was drilled in at distances of 46, 37, and 30·8 cm. apart, the distances between the rows being 30·3 cm.; the manures were 4·8—24 kilos. N per morgen as Chili saltpetre, or 4·8—24 kilos. per morgen as dissolved guano, to which was added sufficient ammonium sulphate to make the nitrogen equal to that in the saltpetre; to both these nitrogenous manures, bone-charcoal superphosphate was added in quantities of 16, 24, and 36 kilos. soluble phosphoric acid per morgen. The results obtained in 1880 show that an increase in the amount of sugar takes place when the plants are planted close together; in most cases, the "quotient" also rises; the prejudicial action of the heavier applications of the nitrate is counterbalanced by the close planting. In 1881 superphosphate was only applied in quantities of 16 kilos. of phosphoric acid, together with varying amounts of saltpetre and sulphate of ammonia (8, 16, 24 kilos. N); the distance between each plant was the same. Again, the advantage of close planting was noted, but not so marked as in the previous year, and the "quotient" is also raised. In a season propitious to the growth of beet, like 1880, it is found that at 46 cm. apart, the crop was but little heavier than when the distance was only 37; in 1881, the narrower distance (37) caused the crop to be considerably heavier. The action of the manures seems to be uncertain, the result being to a great extent dependent on the district; phosphates appeared to have produced but little effect, but in all cases Chili saltpetre lowered the value of the roots.

E. W. P.

**Phosphoric Acid in Arable Soils.** By A. LADUREAU (*Compt. rend.*, 94, 136).—The paper describes a case in which the wheat crops were found to diminish progressively, and to show a marked tendency to be laid down. Analysis proved that the soil, although otherwise well manured, was completely exhausted of its phosphates, and the use of considerable quantities of soluble and insoluble calcium phosphates afforded a satisfactory remedy.

R. R.

**Contributions to the Knowledge of Westphalia Soils.** By J. KÖNIG (*Bied. Centr.*, 1882, 209).—The soils were from the Keuper and Bunt sandstone formation, and contained 2—3 per cent. potash. The percentage of potash increases with that of magnesia. The sub-soil seems to be in a more weathered condition than the surface soil, as far more of it is soluble in acid.

E. W. P.

**Experiments at the Experimental Stations of the Highland Agricultural Society.** By A. P. AITKEN (*Bied. Centr.*, 1882, 169—177).—The objects of the experiments being to ascertain the productive value of the principal manures, the plots ( $\frac{1}{10}$  acre) received 18·1 kilos.  $P_2O_5$ , 13·6 kilos.  $K_2O$ , and 4·5 kilos. N for the trials with roots, and half these quantities were added to those plots on which barley and oats were to be grown, whilst the grass plots were left

unmanured. Ten of the plots were devoted to the detection of the relative action of phosphates dissolved and undissolved, six for potash salts, four for guanos, and three for soluble phosphates of different qualities (10, 20, 30 per cent. soluble  $P_2O_5$ ); another set of plots ( $1\frac{1}{2}$  acre) received the same manures, and served as duplicates.

*Roots in 1878.*—At Harelaw swedes were sown, and at Pumpherstons yellow turnips; the weather being bad, the yield was somewhat low. Comparing the yields from the larger and smaller plots, the results are found to be fairly accordant; the dissolved phosphates produced more than the undissolved, the increase averaging about 10 per cent. Concerning the yield produced by the various phosphates themselves, there is not much difference to be found, bone-meal, by reason of slow assimilation, being somewhat backward. Although the quantity is increased by soluble phosphates, the quality is not improved, for the sp. gr. of the juice of roots grown with crude phosphates is higher, there is more dry matter, and more albuminoids; the ash appears to rise and fall with the greater or less amount of water present. Nitrogenous manures and bone-ash alone give but low results, and Chili saltpetre and ammonium sulphate seem to be of equal value.

*Barley, 1879.*—At Pumpherstons only was manure applied, as it was thought that the Harelaw station was already well enough supplied. The season was cold and damp, so that the ripening period was much delayed. At Pumpherstons, soluble phosphates produced an increased yield of grain over the crude phosphates of 14 per cent., and the amount of straw was also heavier. The equality of yield produced by the superphosphates is to be remarked, while the yield of the crude phosphates is very irregular; this irregularity must be due to the fineness of division, hardness of grain, &c., the extremes are, with bone-ash, 806, with ground apatite 571 kilos. per acre. Of the nitrogenous manures, blood and ammonium sulphate were the best, sodium nitrate failing, probably because of the wet weather; shoddy was useless. Of the guanos, Peruvian was most beneficial, then imitation guano (a mixture of bone-ash, dried blood, and rape-meal). Potash salts were very different in their action. Comparing the barley crop with the roots of the previous season, there is found a great accordance in the rise and fall of the yield of straw and roots on the plots, which is not noticeable when the yields of grain and roots are compared.

The quality of the barley does not seem to have been much affected by the manures, any remarkable difference being in the composition of the ash of the seed, phosphoric acid decreasing in the grain with increasing applications of superphosphates; therefore it is thought that grain required for seed should not be grown under the influence of superphosphate.

*Hay, 1880.*—Italian rye-grass succeeded the barley crop, and no manure was applied, so that the plots at Harelaw received no manure for two years. At this station, two crops of hay were taken, whilst at Pumpherstons there was only one. At both stations great differences were noticed between the plots and their duplicates; whilst at Harelaw the soluble phosphate plots gave an increased yield over the unmanured

of 6—7 per cent., the opposite was the case at Pumpherstons, and here the after-action of the insoluble phosphates was noticeable. Generally those plots which in 1880 produced the heaviest hay crop, had in 1879 brought the lowest yield of roots, and this was most remarkable in the case of bone-meal and shoddy; seeing that fish guano was still backward in its results, no further experiments will be made with it, except after the fat has been removed from it.

*Roots*, 1880.—The  $\frac{1}{12}$  acre plots were sown with yellow turnips (Pumpherstons), and purple-top swedes (Harelaw); the manures were the same as before, with the exception of the addition of crude and dissolved Curaçoa phosphate in place of sodium nitrate and bone-ash. This year again showed the superiority of superphosphates to the amount of 20 per cent., and although the percentage of dry matter is lower, yet the total quantity is higher. E. W. P.

**The Combination in which Nitrogen is most available for Plants.** By E. WEIN (*Bied. Centr.*, 1882, 152—154).—Oats, peas, beans, and soja beans were manured with sodium nitrate, ammonium sulphate, and ammonium nitrate, in artificial soils. In no case was ammonium sulphate of advantage, but rather harmful, and only when it had been oxidised was any good produced. These plants therefore belong to the class of “nitrate plants.” Sodium nitrate appears to bring dicalcium phosphate into solution as easily as ammonium sulphate (see *Chem. Soc. J.*, 1876, i, 733; *Abstr.*, 1881, 457). E. W. P.

**Retrograde Nitrogen.** By H. PELLET (*Bied. Centr.*, 1882, 151).—Pellet corroborates Petermann’s results obtained with blood and leather meal (*Abstr.*, 1882, 331), and communicates information concerning the nitrogen present. The nitrogen in dried blood is soluble in water to the extent of 50 per cent., whereas that in leather is less soluble. The amount of soluble nitrogen should be the measure of the value of the manure, yet water must not be used as the solvent. A manure, “azotin,” containing 11·5—14 per cent. nitrogen which is quite soluble in water, is obtained when wool, silk, and cotton are steamed under pressure and dried; if this manure be mixed with superphosphate, the nitrogen will be rendered insoluble. If, on the other hand, the steamed mass be not dried, but mixed moist with the superphosphate, then the whole mass becomes insoluble. Yet although the azotin is precipitated insoluble, it is considered to be a more valuable manure than leather meal. Azotin is soluble in Joulie’s solution of ammonium citrate, and hence being analogous to reduced phosphate, the term “retrograde” or “reduced” has been applied to this form of nitrogen. To estimate the value of a manure as regards its soluble nitrogen, ammonium citrate should be employed as solvent. E. W. P.

**Composition and Use of Peat.** By J. KÖNIG and DEICHMANN (*Bied. Centr.*, 1882, 150).—König compares the composition of several kinds of peat with that of various straws, and comes to the conclusion that peat is as good a manure as straw, for although wanting in total ash, phosphoric acid, lime, and potash, yet nitrogen is present in larger proportions. Deichmann has practically tested the value of powdered

peat, and finds that for all animals except sheep, it can be used with advantage in preference to straw; in the case of sheep the wool is made too dirty.

E. W. P.

**Manuring with Sea Mud.** (*Bied. Centr.*, 1882, 177—179.)—This material was tried on various farms, and on the whole was found to be advantageous.

E. W. P.

**On Manure Phosphates.** By K. WALTER (*Chem. News*, 45, 49—50).—This is an appeal for the introduction into this country of the determination of assimilable phosphoric acid in place of the determination of phosphoric acid soluble in water. This method has been in use on the Continent for the last four years; the manner of analysis has been fixed by an International Congress of Agricultural Chemists, in Paris. The amount of phosphoric acid dissolved by ammonium citrate that is not dissolved by water is from  $1\frac{1}{2}$ —3 per cent., and this phosphoric acid, which experience has shown to act as beneficially as the acid dissolved by water, is quite lost to the manufacturer by the present mode of analysis. It is also pointed out that those natural phosphates too poor for the manufacture of superphosphate are admirably suited for the preparation of precipitated phosphate with the help of cheap hydrochloric acid. But owing to the present mode of analysis this manure is greatly underestimated, and accordingly but little valued and manufactured in this country.

H. B.

**Manuring with Various Phosphates.** By KROCKER and H. GRAHL (*Bied. Centr.*, 1882, 154—158).—Insoluble and soluble phosphates with bone-meal were employed; these appeared to have no appreciable difference on the yield of oats, but with potatoes the action of soluble phosphate and bone-meal was very marked. Crops of oats and beet were also taken off a field which had been unmanured for many years, and which, having been regularly cropped, was consequently in a poor condition; the oat crop derived no benefit from phosphates alone, but the yield was increased by ammonium sulphate, and when this was combined with phosphates, the yield was still further increased, the best results being obtained from bones, the worst from superphosphate. As regards the material removed by the crops from the soil, it appears that less phosphoric acid and nitrogen was removed from the "phosphate" plots than from the unmanured. All the manure applied increased the yield of beet, but the increase with phosphates alone over the unmanured plot was not great. Phosphates reduced the percentage of sugar, whereas ammonia salts raised the percentage.

E. W. P.

**Manuring with Potash Salts.** By F. FARSKY (*Bied. Centr.*, 1882, 210).—Experiments on buckwheat and sugar-beet with potash salts confirm the results previously published (*Abstr.*, 1881, 1072). Potash salts are of little value on wet land; the chloride and sulphate increase the yield, especially in the presence of superphosphates or lime, whereby the quality is also improved.

E. W. P.

**Manuring Fen Lands with Kainite.** By M. MÄRCKER (*Bied. Centr.*, 1812, 159).—The grass lands received guano superphosphate, ammonium sulphate, and kainite. Phosphates alone produced but little effect, and did not pay for the cost of manuring, neither did the mixture of phosphates and ammonia, although the yield was much increased. The best yield was when kainite was added with the guano, and then only was there any money gain over the unmanured plot, when the expenses of the manures are considered; the additional outlay incurred by the application of ammonium sulphate, although the crop was the heaviest, neutralises any advantage obtained from the value of the greater yield. Ammonia manuring had effect only on the first cut of grass. E. W. P.

**Experiments on Potatoes and Sugar-beet with Potassium Sodium Nitrate.** By HEINE and DRECHSLER (*Bied. Centr.*, 1882, 160–163).—Potassium sodium nitrate (14·7 per cent. N, 12 per cent.  $K_2O$ ) does not produce so good a yield of roots as ordinary Chili saltpetre (15·7 per cent. N), and also it reduces the amount of sugar per root. A like result is obtained with potatoes, both the total yield and the starch being lowered. Drechsler criticises the above experiments, and considers that the apparent failure of the potash salt is due (apart from any possible excess of potash in the soil) to the fact that the nitrogen was 1 kilo. per morgen more on the sodium than on the potassium sodium nitrate plots; further that the amount of potassium applied was insufficient for the wants of the plant. Drechsler also publishes a set of experiments made by himself, which point to a diametrically opposite result to that obtained by Heine; superphosphate was applied with sodium nitrate and with potassium nitrate, plots treated with the first mixture produced 26 centners, those treated with the last 40 centners more potato tubers than the unmanured plot. The amount of starch (calculated from sp. gr.) was raised by potash in the largest size tubers, but lowered in the smallest. Nitrates therefore appear to prejudice the formation of starch; but as the tubers develop, this retarding action of the nitrogen is neutralised more and more by the potash. E. W. P.

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## Analytical Chemistry.

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**Note on a Filtering Syphon for the Separation of Ether, &c.**  
By C. J. H. WARDEN (*Chem. News*, **45**, 69).—This is an adoption of the inverted syphon filter for filtering off the light ethereal layer when extracting cinchona alkaloids. H. B.

**Estimation of Gas Densities.** By H. GOLDSCHMIDT and V. MEYER (*Ber.*, **15**, 137—142).—Two apparatus are described. The one consists of a cylinder 200 mm. high, and about 30 mm. diameter, the top of which ends in a capillary tube for the exit of gases, whilst at the bottom there is another for the admission of gases; this latter is bent round

so as to run parallel with and along the side of the cylinder. This (the cylinder and capillary tubes) fits by means of a cork (cut in halves), into an outer glass vessel, which acts as a bath; the ends of the capillary tubes project beyond the cork, and are bent at right angles, a condenser tube is fitted in the cork of the outside vessel. To use this apparatus, the cylinder is filled with pure dry air, and then heated to the required temperature; the air is now driven out by a current of hydrochloric acid gas, free from air, and is collected in a measuring tube over water. The hydrochloric acid is displaced by dry air, and the gas to be examined is led in until the apparatus is filled with it; this gas is then driven out by a current of air or hydrogen through a weighed tube filled with a suitable absorbent attached to the exit tube, which is afterwards again weighed. In this way we obtain the weights of the gas and of an equal volume of air, the quotient of these weights gives the required density. This apparatus can be used for all temperatures up to and including the boiling point of diphenylamine. For higher temperatures the second apparatus is used; in it the above-mentioned interior cylinder is replaced by a balloon of about 60 mm. diameter, which can be wholly immersed in a crucible of boiling sulphur, or other substance; the crucible is covered with an iron plate, a hole being left for the passage of the capillary tubes, and for the escape of vapour; the ends of the capillary tubes are protected from the heat by another screen. A correction is made for the part of the capillary tubes not in the bath, by measuring the amount of air retained by a piece of the same tube of like length, when it is heated in the sulphur-bath. This second apparatus can be used as an air thermometer, the capacity of the balloon being known, and corrections made for capillarity and expansion of the glass. The efficiency of these apparatus is proved by experiments. D. A. L.

**Indirect Determination of Chlorine and Bromine by Electrolysis.** By L. P. KINNICUTT (*Amer. Chem. J.*, 4, 22—25).—The chlorine and bromine having been precipitated together by silver nitrate, the mixed precipitate is heated in a porcelain crucible at a temperature just sufficient to melt it; and the crucible having been cooled and weighed, a piece of platinum-foil connected with a platinum wire is placed in it so as to rest on the melted silver salts. Dilute sulphuric acid (1 part concentrated acid to 3 parts water by volume) is then poured into the crucible until it is two-thirds full, and a second piece of platinum-foil attached to a wire is placed in the acid solution, care being taken that it does not touch the mixed silver salts. The zinc pole of a two-cell Bunsen battery is then connected with the platinum-foil resting on the silver salts, and the carbon pole with the platinum-foil just mentioned. Decomposition begins immediately, and when it is completed, the reduced silver remains at the bottom of the crucible in the form of a porous mass, which is to be washed, dried, fused, and weighed with the usual precautions. The author finds that this method gives better results than the usual process of reducing the mixed chloride and bromide by heating in hydrogen, or the conversion of the bromide into chloride by heating in a stream of chlorine-gas. H. W.

**Estimation of  $\text{NO}_2$  and  $\text{NO}$  as Ammonia.** By A. GUYARD (H. TAMM) (*Chem. News*, 45, 159).—Nitrogen in all its oxidised forms is converted into ammonia when heated in presence of marsh-gas, and therefore nitrogen as nitroxyl and nitrosyl in organic and inorganic compounds may be readily determined by Will and Varrentrapp's method, if sodium acetate is mixed with the soda-lime. The *modus operandi* is as follows:—1 part of sodium acetate is mixed with 8.75 parts soda-lime, and about one-fourth of the mixture introduced into the combustion tube, the remainder is mixed with the nitro-compound, and introduced into the tube, which is finally filled with ordinary soda-lime.

The operation is conducted in the ordinary manner, the mixture of soda-lime and sodium acetate at the closed end of the tube being heated towards the end of the combustion, in order to free the tube of its ammoniacal contents by a stream of marsh-gas.

This method is absolutely accurate, and by its means the total nitrogen in a substance may be determined in one operation. The determination of the different forms of nitrogen in the same substance, however, requires three determinations:—

- (1.) Estimation of nitrogen as ammonia by sodium and calcium oxalate.
- (2.) Estimation of total nitrogen by soda-lime and sodium acetate. The difference gives nitrogen as oxide.
- (3.) Estimation of total nitrogen after evaporation of the substance with acetic acid to liberate the nitrous acid. The difference between 2 and 3 gives nitrogen as nitrites.

This method is exceedingly useful for the estimation of nitrates and nitrites in mineral waters, manures, &c. L. T. O'S.

**Estimation of Sulphurous Acid in Wine.** By B. HAAS (*Ber.*, 15, 154—159).—The wine is distilled in a current of carbonic anhydride; and the distillate is collected in a suitable apparatus (a bulbed U-tube) containing 30 to 50 c.c. of iodine solution, containing 5 grams pure iodine and 7.5 grams potassium iodide per litre, thus oxidising the sulphurous acid; as soon as the distillate amounts to about half the original volume of the wine used, the contents of the U-tube are washed out, acidulated with hydrochloric acid, precipitated with barium chloride, and the barium sulphate washed, dried, ignited and weighed. This method gives very good results. Wine will absorb as much as 0.36 gram of sulphurous acid per litre when it is shaken in a barrel in which sulphur has been burnt; and if the treatment is repeated, the sulphurous acid will equal 0.5 gram per litre, hence rendering the wine injurious to health, and analysis necessary. Sulphur is burnt in the barrels to prevent the formation of mildew.

D. A. L.

**Test-methods for Soda Works.** By G. LUNGE (*Dingl. polyt. J.*, 243, 418—426).—Referring to the examination of fuel, Lowe's method is recommended, according to which the substance is heated in a platinum crucible over a Bunsen burner, having placed the crucible into a suitable round opening cut into a small piece of asbestos sheeting, the crucible being tilted so that the combustion gases escape at the bottom, whilst air enters through the top. For the estimation

of flue gases the determination of carbonic acid, carbonic oxide, and oxygen is sufficient.

As anemometer Lunge recommends Fletcher's new apparatus for ascertaining air currents. Schäffer and Budenberg's "Thalpotasimeter," and Steinle and Hartung's "graphite pyrometer" are classed among the best pyrometers, although these instruments require correction from time to time. Weber has invented an improved Siemens' pyrometer. This, as is known, is an instrument whereby differences of temperature at a red heat are ascertained as readily as with the use of an ordinary thermometer from the change of resistance which a platinum wire offers to an electric current. Weber has modified the pyrometer so as to make it more practicable.

*Estimation of Nitric Oxide in the Exit Gases of Acid Chambers.*—The best results are obtained when the gas is absorbed in a solution of potassium permanganate. A solution of ferrous sulphate is then added, and the mixture titrated with potassium permanganate. The author gives a sketch of an absorption apparatus resembling Pettenkofer's tube. He, however, prefers to use a large absorption column.

*Analysis of Saltpetre by the aid of Lunge's Nitrometer.*—This apparatus is now largely used in sulphuric acid, nitric acid, and glycerol works for the determination of acid mixtures, nitroso-compounds, &c. By an alteration in the form of the nitrometer, the author has succeeded in determining nitric acid in saltpetre. A description of the apparatus without the accompanying drawing would not be understood. The results are satisfactory. The presence of chlorides or organic substances (which may be present in saltpetre) does not interfere with the reaction.

*Indicators for Alkalimetry.*—The author has compared a number of indicators with one another, but has been compelled to abandon the use of all except the "dimethylaniline orange" indicator, which enables us to titrate alkaline carbonates and sulphides in the cold. For titrating, mineral acids should be used.

Degener has recommended a new reagent for titrating caustic alkalis, their salts (even carbonates) assuming a different colour from that produced with free alkalis. For the preparation of the indicator, called "phenacetolin," phenol, concentrated sulphuric acid and acetic anhydride are mixed in equivalent quantities and heated for some time in a flask fitted with an upright condensing tube. By repeated treatment with cold water, phenacetolin is separated. It is used in alcoholic solution, dissolves in caustic alkalis with a pale yellow colour, and forms permanent red compounds with alkaline carbonates and alkaline earths.

D. B.

**Detection of Traces of Silver in Lead Ores.** By J. KRUTWIG (*Ber.*, 15, 307—308).—The method proposed is based on the golden precipitate produced when soda is added to a mixed solution of lead and silver salts; this precipitate contains both silver and lead, probably a silver plumbite or plumbate; it is insoluble in water and in soda solution, soluble in ammonia. The reaction is very delicate. In order to estimate the silver in galena, the ore is fused with potassium hydrogen tartrate, soda and borax; a regulus of lead is obtained, which

contains all the silver present in the ore, together with iron and sulphur. The lead is dissolved in concentrated nitric acid, and soda is added, which throws down a golden-brown precipitate, consisting of lead and iron hydroxides and the silver plumbate. The latter is dissolved by ammonia, the solution evaporated, and the reprecipitated lead plumbate dissolved in acetic acid; the lead is precipitated from the solution by sulphuric acid, and the silver in the filtrate by hydrochloric acid.

Analyses are quoted to show the accuracy of the process.

V. H. V.

**Estimation of Magnesium in Urine by Titration.** By F. KRAUS (*Zeitschr. f. Physiol. Chem.*, **5**, 422—426).—Tri- and di-sodic phosphates colour cochineal tincture violet: on adding acid, the colour changes almost instantly to yellow-red, *i.e.*, so soon as the fluid contains only monosodium phosphate. According to Stolba, this holds good for insoluble compounds, and it is possible to found a volumetric method on it and to estimate the amount of ammonium and magnesium phosphate after precipitation and thorough washing with sulphuric acid of known strength. The author found that sodium phosphate and ammonium magnesium phosphate yielded very consonant results when treated in this way. The method applied to urine was as follows:—The lime and magnesia were precipitated together by adding ammonia and ammonium oxalate. The precipitate was then washed with water containing ammonia; finally with alcohol, then dissolved in 50 to 70 c.c. of decinormal sulphuric acid, and titrated back with soda.

The values obtained agreed very well with one another, *e.g.*, in 250 c.c. of urine 0.0360 gram and 0.0358 gram magnesia were found; in another sample of 300 c.c. 0.0298 gram and 0.0294 gram were found. The results were, however, invariably 5.7 to 10 per cent. above those found by weighing.

W. N.

**Note on the Volumetric Estimation of Zinc by Titration with Potassium Ferrocyanide.** By R. W. MAHON (*Amer. Chem. J.*, **4**, 53—55).—A method of estimating zinc by means of a standard solution of potassium ferrocyanide was described by Fahlberg in 1874 (*Zeitschr. anal. Chem.*, **13**, 379; this Journal, 1875, 665).

In applying this method to the estimation of zinc in ores, &c., the metals precipitable by hydrogen sulphide from acid solution are first removed; the iron is separated from the filtrate by ammonia in the usual way; the ammoniacal filtrate is then made acid with hydrochloric acid, and the titration with ferrocyanide is performed upon the acid solution. In this part of the process, according to Fahlberg, the presence of manganese does not interfere with the result. Mahon, on the other hand, finds that the method as described by Fahlberg is not applicable in presence of manganese, inasmuch as the manganese and zinc are precipitated together by potassium ferrocyanide, and any precipitation of manganese by oxidation, as for example, by the addition of bromine-water, would be sure to throw down considerable quantities of zinc at the same time. In order, therefore, to obtain a solution for titration when manganese and zinc occur together, the zinc must be precipitated by hydrogen sulphide from a solution con-

taining a considerable excess of acetic acid, and the precipitate redissolved in hydrochloric acid; the titration may then be performed on the resulting solution.  
H. W.

**Analyses of Crude Zinc.** By O. GÜNTHER (*Dingl. polyt. J.*, **243**, 347).—100 grams zinc borings (or if the zinc is very impure 25 grams) are treated in a litre flask with 100 c.c. distilled water. Hydrochloric acid is then added in gradually decreasing quantities to effect a quiet solution. In order to prevent lead, copper, and cadmium being dissolved, the addition of hydrochloric acid should be limited, so that a notable quantity of zinc remains undissolved. The last addition of acid is made at the end of the second day, and to make sure that the solution contains only zinc and iron, it is necessary to keep the mixture at rest for at least two days. It is then filtered, the residue washed with lukewarm water by decantation, and the filtrate A reserved for further treatment. The residue is dissolved in pure nitric acid, the solution evaporated to dryness, moistened with nitric acid, taken up with water, allowed to settle, and filtered off. The precipitate should be tested for lead, as in the presence of a highly sulphurous zinc, lead sulphate may separate. The filtrate is evaporated with enough concentrated sulphuric acid to expel all the nitric acid. Water is then added after cooling, and the lead sulphate determined.

In the filtrate, copper and cadmium are precipitated by sulphuretted hydrogen, and estimated in the usual manner. The excess of sulphuretted hydrogen is removed from the filtrate, which is then added to filtrate A. The iron is oxidised with nitric acid and bromine, the hot liquid treated with an excess of ammonia, the iron precipitate filtered off whilst hot, and washed with hot water. It is then redissolved in hydrochloric acid, the solution saturated with ammonia, and the iron determined in the precipitate.

For the determination of sulphur, antimony, and arsenic, 100 grams (to 25 grams) of the sample are dissolved in dilute sulphuric acid, adding a small quantity of chemically pure zinc at the end of the operation. The gas evolved is passed through a solution of cadmium cyanide in potassium cyanide, which retains all the sulphur, so that it may be estimated as cadmium sulphide. The gas is then passed into a solution of silver nitrate; if arseniuretted hydrogen is present, metallic silver is deposited, whilst antimoniuiretted hydrogen forms silver antimonide. The precipitate in the silver solution is dissolved in concentrated nitric acid, evaporated to dryness, the residue dissolved in dilute nitric acid, the precipitated antimony antimonate collected on a filter, and the silver determined in the filtrate. By deducting from the total quantity of silver that combined with antimony, the quantity of silver precipitated by arsenic is ascertained.

D. B.

**Volumetric Estimation of Copper and Lead.** By P. CASAMAJOR (*Chem. News*, **45**, 167).—These processes are founded on the easy agglomeration of copper and lead sulphides when agitated in presence of an alkaline tartrate.

To the copper solution, an alkaline solution, of Rochelle salt is

added, slightly in excess of that required to dissolve the precipitate; an intense blue solution is thus obtained, which is heated almost to boiling point in a porcelain dish; a standard solution of sodium sulphide is then added from a burette, when an intense black-brown precipitate is formed, which on thorough stirring agglomerates to a coarse curdy mass, which quickly settles, leaving a colourless solution. After every addition of sulphide, the solution must be well stirred; at the beginning, the brown cloud is very intense, but towards the end of the reaction it is comparatively slight, by well stirring the liquid, however, it settles, leaving the liquid perfectly clear. It is necessary, when the reaction is nearly finished, that the solution should be clear before adding more sulphide, in order that the slightest turbidity may be detected, this being an easy matter on the white ground of the basin. 1 part of copper in 30,000 gives a distinct turbidity. The same process may be applied to the estimation of lead, which is easily separated from other metals as sulphates, and this is dissolved in the alkaline tartrate.

Copper is separated from other metals as thiocyanate, in which form it is dissolved in nitric acid, &c., and estimated as above, or it may be precipitated from an alkaline tartrate solution by glucose, and the cuprous oxide dissolved in nitric acid. This process may also serve as an indirect method for the determination of glucose and cane-sugar.

The tartrate solution is prepared by dissolving 173 grams Rochelle salt in 480 c.c. soda solution (sp. gr. 1.14), and diluting to 1 litre.

The sodium sulphide is standardised according to Pelouze's method, by dissolving 1 gram pure copper in nitric acid, adding 40—50 c.c. ammonia; the solution is then boiled, and the sulphide added until the colour of the copper solution disappears. The sodium sulphide solution keeps very well in well stoppered bottles.

L. T. O'S.

**Analyses of Iron Ores containing both Phosphoric and Titanic Acids.** By T. M. DROWN and P. W. SHIMER (*Amer. Chem. J.*, 4, 1—8).—Contains detailed descriptions of processes scarcely admitting of abstraction.

H. W.

**Detection of Tin in Presence of Antimony.** By M. M. P. MUIR (*Chem. News*, 45, 69).—The precipitated sulphides of the arsenic group are warmed with concentrated hydrochloric acid, and the solution diluted and filtered from the arsenic sulphide. About three-quarters of the solution is boiled for at least 10 minutes with copper turnings (free from tin), the solution poured off and tested with mercuric chloride for stannous chloride, to which state the stannic chloride has been reduced. The rest of the hydrochloric solution is tested for antimony with platinum and zinc.

H. B.

**New Method of Testing for Chloroform in Cases of Poisoning.** By D. VITALI (*Gazzetta*, 1881, 489—496).—This method is based on the resolution of chloroform vapour at a red heat into carbon, hydrogen chloride, and free chlorine;  $\text{CHCl}_3 = \text{C} + \text{HCl} + \text{Cl}_2$ ; the formation of copper chloride by the action of the resulting gaseous

mixture on metallic copper; and the violet-blue colour imparted by that compound to flame. To apply this method, the fluids and organs of the body in which chloroform is known to accumulate most abundantly are distilled with water, and a portion of the distillate is introduced into a hydrogen-generator, the gas evolved from which is burning from a platinum-jet, and has been previously shown to be free from any compounds capable of interfering with the test, by remaining unaltered as to colour when a copper wire is held in the flame. If then the copper wire be again introduced into the flame after the introduction of the distillate obtained as above, and a blue coloration of the flame be thereby produced, the presence of chloroform in the distillate may be safely inferred. Another method of testing for chloroform is to pass the gas into a mixture of potassium hydroxide and thymol, whereupon, if chloroform is present, the liquid will assume a red colour, especially on heating. The same method may also evidently be used as a test for thymol, viz., by passing the gas into a mixture of potash and chloroform. H. W.

**New Method of Estimating Phenol.** By GIACOSA (*R. Accad. di Torino*, 16, 565—567; *Gazzetta*, 1881, 541).—Instead of the method of estimating phenol commonly employed in clinical researches, based on the precipitation of trinitrophenol by an excess of bromine-water, the author proposes to purify it, and weigh it after drying. He also recommends a volumetric method still more exact and expeditious. Bromine-water of any strength is first titrated with a normal solution of phenol (1 per cent.), the point of saturation being determined by means of a solution of potassium iodide in starch, which is capable of showing the presence of the slightest excess of bromine.

The phenol solution to be tested is poured into the titrated bromine-water, stirring quickly with a glass rod, and leaving the precipitate to settle down. As long as any excess of bromine is present, the supernatant liquid will be yellow and turbid, but on adding the phenol solution, drop by drop, the point of saturation will be indicated by the liquid becoming clear. H. W.

**Comparative Estimation of Fat in Milk by Weight; the Lactobutyrometer, and a New Aræometric Method by Soxhlet.** By E. EGGER (*Zeitschr. f. Biol.*, 17, 110).—The author examined 18 samples. Soxhlet's method gave differences only in the second place of decimals compared with the weight analyses. The lactobutyrometer of Tollens and Schmidt gave important differences in the first place, amounting to a mean of 0.36 per cent. fat. W. N.

**Estimation of Urea by Sodium Hypobromite.** By J. R. DUGGAN (*Amer. Chem. J.*, 4, 47—49).—The author, after noticing that Knop's method of estimating urea by the quantity of nitrogen evolved on decomposing that compound by an alkaline hypobromite, does not, for the most part, give more than 92 per cent. of the total quantity of nitrogen that should be liberated, and moreover that the amount of error is not constant, proceeds to examine the conditions necessary for the attainment of greater accuracy. He finds that the largest quantity



of nitrogen is liberated by a solution containing sodium hydroxide and bromine in about the proportion recommended by Knop, but considerably more concentrated. A solution containing 20 g. NaOH and 5 c.c. bromine in any quantity of water between 50 and 100 c.c. gave fairly uniform results, and from 5 to 10 per cent. more nitrogen than more dilute solutions: still the amount of nitrogen liberated never exceeded 92 per cent. of the whole. Much better results are obtained by first mixing the solution of urea with caustic soda, and then adding the bromine, so as to form the hypobromite in presence of the urea. By experimenting in this manner, the author obtained, with solutions containing 1, 2, and 3 per cent. urea, quantities of nitrogen varying from 99.02 to 99.91 per cent. of the whole, the last result being obtained with a solution containing 2 per cent. of urea.

The soda-solution is made by dissolving 20 g. sodium hydroxide in 100 c.c. water, and with each 20 c.c. of this liquid there should be used 1 c.c. bromine. The measuring out of the bromine may be facilitated by introducing a few drops of water into the tube, which will float on the top, and prevent to a great extent the escape of bromine-vapour.

H. W.

**Quantitative Estimation of Urea by Alkaline Hypochlorites and Hypobromites.** By T. G. WORMLEY (*Chem. News*, 45, 27—28).—An historical account of this process is given. The author then shows that under the following conditions the whole of the nitrogen is uniformly eliminated:—(1.) The reagent must be freshly prepared; 100 grains of soda are dissolved in 250 c.c. water, and to the cooled mixture is added 25 c.c. bromine. In applying the reagent it is diluted with a volume and a half of pure water. (2.) The urea solution should be added in small portions to the reagent, and the effervescence allowed to cease before any further addition of urea. (3.) The amount of urea operated on should not exceed 1 part to about 1200 parts of the diluted reagent.

H. B.

**Liebig's Method of Estimating Urea, and its Modifications.** By M. GRUBER (*Zeitschr. f. Biol.*, 17, 78—112).—The author recognises four methods of titrating urea. (1.) The original method of Liebig, in which the mixture of urine and baryta is not neutralised during the addition of the mercuric nitrate solution, and in which the end reaction is determined by allowing a drop of the mixture to run into a drop of a saturated solution of sodium carbonate on a white tile. 10 c.c. of Liebig's solution—made by dissolving 71.5 grams of mercury acid, and diluting to a litre—being equivalent to 0.1 gram urea. (2.) The method of Voit and Neubauer; in this again the mixture is not neutralised, and the end reaction is determined as before, 10 c.c. of Liebig's solution, according to this method, being equivalent to 0.1183 gram urea. (3.) Hoppe-Seyler's method. In this the mixture of urine and mercurial solution is from time to time neutralised, so as to maintain a tolerably constant degree of alkalinity—the end reaction being determined as before. 10 c.c. of Liebig's solution, if this method be used, are equivalent to 0.1031 gram urea. This method gives very consonant results; the burette can be read to 0.1 c.c.

(4.) Pflüger's method, in which in addition to the neutralisation, correction is made for the continual dilution of the fluids; under these circumstances the author finds 10 c.c. of Liebig's solution to be equivalent to 0.099 gram urea; he is therefore of opinion that Liebig's original method is good, and the original correction for dilution perfectly correct. A portion of the paper is devoted to a criticism of Pflüger's work on the subject. W. N.

**Titration of Urea.** By E. PFLÜGER (*Pflüger's Archiv.*, **25**, 292—298).—This paper is entirely critical and polemical. The author insists on the importance of strict attention to the method of adding the mercuric nitrate solution which he laid down in a previous paper. W. N.

**Estimation of Tannin and Cœnogallic Acid in Wines.** By F. JEAN (*Compt. rend.*, **94**, 735—736).—100 c.c. or 50 c.c. of the wine is evaporated on a sand-bath to small bulk, mixed with silica and dried at 60—70°. The mass is then powdered and extracted with ether mixed with a small quantity of ethyl chloride. The ethereal solution is evaporated to dryness on a water-bath and the residue dissolved in 100 c.c. of water. In 10 c.c. of this solution, the tannin and cœnogallic acid are estimated by means of iodine in solution as previously described (this vol., 430). The remainder is treated with a slight excess of powdered skin to precipitate the tannin, allowed to stand for some hours, filtered, and 10 c.c. of the filtrate titrated by means of iodine. This gives the amount of cœnogallic acid. The difference between this and the first quantity gives the amount of tannin. C. H. B.

**The Condition of Sulphur in Coal, and its Relation to Coking.** By T. M. DROWN (*Amer. Chem. J.*, **4**, 8—16).—The author, in 1880, described a method of determining sulphur in metallic sulphides by means of a solution of sodium hydroxide saturated with bromine (*Abstr.*, 1881, 645), and gave determinations of sulphur in coal, thus made, which, though agreeing closely with one another, nevertheless fell far short of the total sulphur in the coal, leading to the inference that the sulphur not oxidised by the bromine-solution was an organic constituent of the coal, and could be determined only by a process which would oxidise the coal completely. The present paper gives further results of the application of the bromine-process to coal and coke, with the object of determining, if possible, the effect of coking on the amount and condition of sulphur in coal. The total amount of sulphur was estimated by Eschka's method of heating with magnesia and sodium carbonate, and oxidising the aqueous extract of the product with bromine. The coals used were from Pennsylvania and Virginia. The results showed that there is in all cases an excess of sulphur over what is necessary to form pyrites with the iron, and that on the other hand, the quantity of sulphur determinable by bromine is not sufficient to form pyrites with all the iron. This would seem to indicate that the sulphur is present in these coals, both as pyrites and as an organic constituent of the coal, and that the iron is

present, in combination partly with sulphur, partly with silica, and other inorganic constituents of the coal.

In coals containing a considerable amount of sulphur, both as metallic sulphide and as an inherent constituent of the coal, and at the same time low in volatile ingredients, the elimination of sulphur in coking appears to be limited to a portion of that which exists as pyrites, the organic sulphur—if so it may be called—not being affected by the process. In other coals, low in pyrites and higher in volatile matters, there was an elimination of organic sulphur to the amount of 20 to 45 per cent. Admitting the presence of organic sulphur in coke, it is probable that no plan for its removal would be effective which would not involve the destruction of the coke itself. The method of analysis given in this paper affords the means of distinguishing between the organic and inorganic combinations of sulphur in coke, and thus of determining the feasibility of its desulphuration. H. W.

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## Technical Chemistry.

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**Decolorising Properties of Hydrogen Sulphide.** By BELLUCCI (*R. Accad. dei Lincei*, 5, 120; *Gazzetta*, 1881, 545).—From experiments on the action of hydrogen sulphide on various vegetable tinctures, the author has arrived at the following conclusions:—1. Hydrogen sulphide possesses powerful decolorising properties, varying however according to the substance acted upon. For some substances (litmus, indigo) its decolorising power is greater than that of sulphurous acid; for others (the colouring matter of roses) it is less. 2. The decolorising power is due to the formation of a somewhat unstable compound of the sulphur contained in it with the various colouring matters, this compound being sometimes precipitated, and then slowly decomposed by the joint action of water and atmospheric oxygen. H. W.

**Potash from Bamboo.** By R. ROMANIS (*Chem. News*, 45, 158).—It has been proposed by the Forest Department of British Burmah to extract potash from the ashes of the bamboo shoots. A sample gave the following results on analysis:—

K <sub>2</sub> O.	Na <sub>2</sub> O.	KCl.	SiO <sub>2</sub> .	CO <sub>2</sub> .	SO <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub> .	H <sub>2</sub> O.
32·54	0·98	18·72	16·95	8·07	2·71	1·10	19·43 = 100·50
							L. T. O'S.

**Influence of Manganese on the Strength of Iron.** (*Dingl. polyt. J.*, 243, 333—335).—The conclusions arrived at may be summarised as follows:—(1.) It is very difficult to obtain a mixture of different kinds of iron or alloys. (2.) Manganese is oxidised with great ease and disappears from the alloy. (3.) In order to obtain a uniform product in the production of “flowing iron,” special stress

should be laid on the mode of mixing. (4.) If iron of great strength is required, the quantity of manganese must not exceed 3 per cent.; the best results were obtained with 0.95 per cent. of carbon and 0.5 to 0.6 per cent. of manganese. (5.) The contraction is the greatest when the iron contains 0.6 per cent. of carbon and 0.3 to 0.32 per cent. of manganese. (6.) The maximum modulus of elasticity is obtained with 0.29 per cent. of carbon and 0.24 per cent. manganese, and (7.) The greatest limit of elasticity with 0.43 per cent. carbon and 1.19 per cent. manganese. No practical value is attached to these results, as they are influenced by the other ingredients present in the iron, especially phosphorus. D. B.

**Copper-plating.** By F. WEIL (*Compt. rend.*, 94, 157).—The author, referring to the description of his process of copper-plating in the *Ann. Chim. Phys.* [4], 44, insists on the employment of an organic acid as playing the most important part in his method. R. R.

**Recovering Glycerol from Spent Soap Leys.** By H. FLEMING (*Dingl. polyt. J.*, 243, 330—333).—The author proposes to subject the spent leys to dialysis. He shows that the four soap works at Neuwied alone produce annually about 1500 tons of waste liquors containing about 75 tons of glycerol. The percentage of glycerol in the leys varies from 0.92—7.8, and in order to recover the same by distillation it is necessary to remove the salt contained therein. The most effectual means of doing this is to subject the leys to osmotic action. The leys are concentrated in suitable pans with steam heat, and then neutralised with sulphuric acid. The quantity of acid required depends on the amount of sodium carbonate present in the leys. As owing to the violent evolution of carbonic acid it is difficult to obtain a perfectly neutral solution, it is preferable to add a slight excess of acid which, after the precipitation and separation of the sodium sulphate, is removed by lime. The liquor is re-evaporated with steam, a further (small) quantity of sodium sulphate and chloride crystallising out on cooling. It is now osmosed, and leaves the osmometer sufficiently free from ash constituents to be distilled after concentration, either *per se* or in conjunction with crude glycerol obtained in the manufacture of stearic acid. The loss of glycerol by distillation is very small, and as to the purity of the resulting product, it is shown that it fulfils all the requirements necessary for the successful preparation of dynamite. The great feature of the process is that, unlike molasses, the liquor treated does not attack parchment paper. A large quantity of glycerol remains in the osmose water, which may be recovered by concentrating and distilling the liquid. D. B.

**Investigation of Beet-root and Sugar.** (*Dingl. polyt. J.*, 243, 407—414).—Nord has determined the quantity of sugar in "lime mud" according to Schiebler's extraction method (*ibid.*, 240, 381). Having made a moisture determination, the sample is mixed thoroughly with water and saturated with carbonic acid. A dark-coloured brown solution is thus produced, containing in solution those foreign substances which are separated from the juice by the lime treatment.

The complete extraction of the mud is effected very easily; it is, however, more difficult to render the caustic lime or sugar-lime present in the mud inactive. Numerous experiments made by Nord with lime mud of different constitution show that the desired effect is obtained, and the method simplified by the addition of ammonium carbonate instead of carbonic acid. In this case, the solution has a pale yellow colour, and does not contain any of the foreign substances separated by the lime extraction. The solution should be neutralised with acetic acid before clarification with lead acetate, otherwise the results obtained, when the solution is examined by polarised light, are too low. 20 grams of the mud are mixed intimately with 0.2 gram (or more) of ammonium carbonate dissolved in water, and 20 grams sand. The mixture is dried, broken up in pieces of the size of a pea, transferred to an extraction tube, and extracted with 15 grams water and 20 grams alcohol in the usual manner.

Degener has investigated the reducing power of various kinds of sugar on alkaline solutions of copper. It cannot be supposed that basic sodio-cupric tartrate,  $\text{Cu}_3\text{Na}_2(\text{C}_4\text{H}_4\text{O}_6)_2\text{O}_2 + 7\text{H}_2\text{O}$ , is contained in Fehling's solution in its ordinary state of concentration, as this salt cannot be obtained from it. By mixing a solution of 34.64 grams cupric sulphate in 0.5 litre water with a solution of 173 grams Rochelle salt in 0.5 litre water, the precipitate of cupric tartrate does not form immediately, but requires some time. As Fehling recommends to mix the copper solution with Rochelle salt dissolved in alkali, basic sodio-potassio-cupric tartrate, sodium sulphate, and sodium tartrate cannot be produced. The products formed are sodium sulphate and cupric hydroxide. The latter is kept in solution by Rochelle salt, and probably forms a double salt which, however, is as yet unknown, but its composition and chemical properties must differ from the salt of the above formula. Fehling's double salt is reduced with greater difficulty than that used by Degener, so that by the influence of free alkali the reduced sugar loses part of its reducing power before the unknown double salt can come into play, which circumstance explains the uncertainty of the Fehling solution. However, it was found, by digesting a weighed excessive quantity of cupric tartrate in warm soda ley for some time until the alkaline reaction had disappeared, filtering, and weighing the insoluble residue, that for 4 mols. sodium hydroxide, 3 mols. cupric tartrate were dissolved corresponding with the equation  $3\text{C}_4\text{H}_4\text{O}_6\text{Cu} \cdot 3\text{H}_2\text{O} + 4\text{NaHO} = \text{Cu}_3\text{Na}_2(\text{C}_4\text{H}_4\text{O}_6)_2 \cdot 7\text{H}_2\text{O} + \text{Na}_2\text{C}_4\text{H}_4\text{O}_6 + 4\text{H}_2\text{O}$ , 400 c.c. normal soda solution (= 16 grams NaHO) dissolved 80.2 grams cupric tartrate, the solution obtained forming the double salt in question. It is possible to impart to Fehling's solution the properties characterising the above solution of basic sodio-cupric tartrate by dissolving the prescribed quantity of cupric sulphate in the smallest possible quantity of water, and adding the quantity of Rochelle salt required by the equation  $2\text{CuSO}_4 + 5\text{H}_2\text{O} + \text{KNaC}_4\text{H}_4\text{O}_6 + 4\text{H}_2\text{O} = 2\text{CuC}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O} + \text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O} + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}$ , also dissolved in a very small amount of water. The mixture is kept at rest for some time.

Degener has also made comparative estimations of the quantity of sugar in beet. He mentions that Scheibler's method of extracting

with alcohol is most trustworthy. When the juice is extracted by means of hydraulic pressure, it is impossible to obtain concordant results, as the degree of pressure influences the amount of moisture left in the residue, and consequently affects the quotient of polarisation. D. B.

**Experiments on the Recovery of Sugar from Molasses.** By F. KROUPA and JÜNEMANN (*Bied. Centr.*, 1882, 201—203).—Kroupa finds that the mass of sugar and lime on the parchment dialyser hinders the osmotic action by blocking up the pores of the paper.

Jünemann states that he introduced and patented the strontian process, and has examined other methods, notably that of Duncan, in which the potash is removed as alum; further investigations have enabled him to introduce a method which only requires for apparatus a filter press and separating pans. E. W. P.

**The So-called "Flux" of Soap.** (*Dingl. polyt. J.*, 243, 414—418).—In hard soap, the flux appears in the form of a fibrous opaque separation, and by its presence the homogeneous mass acquires a pleasing effect. It may be separated from the mass by treatment with a large quantity of water, and forms a skeleton of shining, white, fibrous, slightly adhesive masses, exhibiting after drying a mother-of-pearl lustre.

In 1873, Fricke made some investigations in reference to this substance, and recently Dege has taken up the subject. A very fine white soap is now brought into the market, prepared from tallow and cocoanut oil, and exhibits the above described appearance in a very striking manner. The flux was separated by lixiviating the soap with a large quantity of water, pressing the residue, treating it with salt water, then boiling out with water, and finally extracting with hot alcohol. The residue forming the flux of the soap is perfectly white, fibrous, has a mother-of-pearl lustre, and is insoluble in water at all temperatures. It dissolves in a solution of soda-soap, its solubility depending on the concentration and the temperature of the soap solution. This circumstance explains the development and formation of the flux. The boiling-hot finished soap holds the whole of the mother-of-pearl-like body in solution, whilst on cooling in frames a portion separates in the form of silky fibres, forming the flux. A sample of cocoanut-oil soap was analysed, giving 76·27 per cent. fatty acids, 8·21 per cent. soda, 0·30 per cent. lime, and 15·22 per cent. water. The quantity of 0·3 per cent. of lime corresponds with 3·8 per cent. of lime soap, its presence being explained by its existence in commercial sodium carbonate, which is still largely used in soap making. In conclusion, it is mentioned that it would be imprudent to attribute the flux of soap solely to the formation of a crystallised lime salt of the fatty acid, although it may be fairly assumed that generally the flux owes its origin to this salt. D. B.

**Production of Colouring Matters by the Action of Aromatic Nitrosubstitution-products on Phenols and Polyatomic Alcohols in the Presence of Dehydrating Agents.** By H. BRUNNER

(*Ber.*, 15, 174—179).—By the action of nitrobenzene on resorcinol and of nitroalizarin on erythrol and sugar, in presence of strong sulphuric acid, the author has obtained several very beautiful colouring matters, soluble in alkalis; the solutions (from resorcinol) show fluorescence. With bromine, they yield brominated derivatives. The description of these substances will be published in a future communication.

D. A. L.

**Method of Printing and Burning-in of Names, Monograms, &c., on Glass and Porcelain.** By J. B. MILLER (*Dingl. polyt. J.*, 243, 335—337).—The author attributes the failure of trials made with a view of printing directly on glass to the difficulty of preparing a colour sufficiently concentrated to leave a good impression when burnt in. Hitherto gold, platinum, and silver, and a few expensive pigments have been used exclusively, but the difficulty is now overcome by the following process:—Thick oil used for painting, or Venetian turpentine and some French oil of turpentine, are mixed thoroughly with a spatula on a small smooth (ground) glass plate. The pigment should be tested before using it, and when subjected to fusion should have the property of being burnt in completely. This operation may be accelerated by the addition of fluxes to the mass. The pigment is placed on a smooth stout glass plate, rubbed down with a glass pestle, then dried at a moderate heat and ground to a very fine powder. It is now ready for use. The stamp used for printing consists of vulcanised caoutchouc. The glass to be printed having been cleaned, the stamp is dipped into the thick oil, and pressed gently against the glass. The prepared colour is then put on the printed place with a fine hair brush, and the excess of colour removed with a clean hair brush. The burning in is effected in the usual manner. Porcelain, &c., is treated in a similar way.

D. B.

**Analysis of Corn Ergot or Corn Smut (*Ustilago Maidis*).** By H. B. PARSONS (*Pharm. J. Trans.* [3], 12, 810—812).—The analysis of this substance, which is used as a substitute for ergot, was made with the view to determine its constituents and probable medicinal properties.

*Proximate Analysis.*

Moisture.	Sand.	Sol. ash.	Insol. ash.
8.88	4.01	3.86	1.61

The *etheral extract*, consisting of fixed oil, amounted to 4.20 per cent.; the *alcoholic extract* to 9.84; and the *aqueous extract* to 6.55; cellulose, 2.56. Besides this there were starch isomerides, 12.87; albuminoids, 12.95; and other substances soluble in alkalis and hypochlorites, 32.67.

The most important of the constituents are:—

(1.) The fixed oil, which is apparently a glyceride of orange-yellow colour, peculiar odour, acrid taste, soluble in ether, and sparingly in alcohol. It resembles the oil of ergot, but is found in much smaller quantities in corn smut.

(2.) A volatile base of a peculiar musty or fish-like odour; it has



an alkaline reaction, but is not trimethylamine, nor does it respond to the usual reactions for the alkaloids.

The alcoholic extract when evaporated yields about three-fourths of the residue to water, giving a yellow solution of acid reaction, and peculiar bland taste. The portion insoluble in water consists of the albuminoid matter, a light yellow resin, and a red-brown colouring matter. The two latter are soluble in ammonia, from which solution the resin is precipitated by hydrochloric acid.

The aqueous extract has a pale yellow colour, a faintly acid reaction, and leaves a hygroscopic residue on evaporation. During evaporation, the albuminoid matter separates out. On treating the concentrated extract with alcohol (90 per cent.), the albuminoid matter and a small amount of gum separate out; and on filtering and treating the filtrate with a further quantity of alcohol, a yellowish-white precipitate separates out, consisting probably of sclerotic acid; the term, however, is used provisionally, although the acid was determined by the method recommended by Dragendorff for the analysis of ergot. It contains nitrogen; when dried it is of a red-brown colour, nearly tasteless, and leaves a considerable ash on ignition. The filtrate from the sclerotic acid yields a residue of a yellow colour and acid reaction.

Corn smut contains no true organised starch, the starch isomerides, therefore, are probably easily decomposable cellulose.

The 32.67 per cent. "other dissolved substances" consist chiefly of the real organic structure of the spores, corresponding to the cellulose of ordinary plant organisms. Alkalis failed to remove all soluble matter, large portions of which were dissolved by Labarraque's solution, which took up a considerable quantity of the black residue, bleaching it at the same time, and leaving pure cellulose undissolved.

The portion of the corn smut corresponding with the true fibre of the ordinary plant, is probably dissolved by caustic soda and the hypochlorite solution, the insoluble cellulose being derived from extraneous woody fibres present in the sample. The constituents of medicinal value appear to be the fixed oil, the volatile amine, and the sclerotic acid.

L. T. O'S.

**German Vaseline.** (*Pharm. J. Trans.* [3], 12, 727.)—Vaseline or petroleum ointment is prepared from American petroleum residue, or from crude ozokerite, known as "mountain tar," from Alsace and Galicia. Two processes may be employed for its manufacture.

(1.) The oil is heated at 30° with 10 per cent. sulphuric acid, stirred for half an hour, and the carbonised portion allowed to separate. The clear oil is treated with aqueous potassium dichromate solution, and after washing is heated by steam at 80°, mixed with 10 per cent. of granular spodium, and after the spodium has separated, the liquid portion is filtered through filters heated by steam.

The residue from the acid treatment is neutralised with lime, and used for manure purposes, whilst the spodium residue is subjected to hydraulic pressure, the oil being filtered and the solid residue used in the next operation.

(2.) The petroleum residue is passed through 12 or 15 charcoal filters, such as are used in sugar refineries, when the colour changes

from a brownish-black to a wine-yellow. To render the oil colourless, double the number of filters are required. The sp. gr. decreases with the colour, and when colourless the sp. gr. is stationary. After the oil has been freed from all bituminous matters it is transferred to a "duplicator," where it is subjected to superheated steam ( $250^{\circ}$ ) until no further change takes place, when it is filtered and filled into cans. The objection to this process is the rapid exhaustion of the animal charcoal, which can decolorise only a small percentage of its own weight of raw material, but this may be increased by partial purification of the oil with sulphuric acid before filtration. The filters are restored to activity by treatment with superheated steam at  $400-500^{\circ}$ . The vaselin thus obtained is a white, odourless, tasteless ointment, of sp. gr. 0.848, melting to a clear colourless liquid. It is sparingly soluble in cold strong alcohol, completely in hot, and separates out from the solution on cooling; with benzene and ether it behaves similarly. Boiling dilute sulphuric or nitric acid does not act on vaselin, but sulphuric acid (1.820) colours it greyish-black, and fuming nitric acid yellowish-red. When heated under pressure with oxygen for several hours, it undergoes slight oxidation.

L. T. O'S.

**Conversion of Molasses Waste into Gas.** By E. ERNST-BEESEN-LAUBLINGEN (*Bied. Centr.*, 1882, 58).—The molasses waste is to be mixed with 25 per cent. of its weight of dry peat, and 3 per cent. of quicklime, and 6 per cent. fatty oil. The peat prevents the foaming in the retort, the lime aids elimination of ammonia, and the oil renders the gas richer in hydrocarbons.

E. W. P.

**Applications of Tannin.** By J. KOEHLIN (*Chem. News*, 45, 112—113).—The author in the first part of the paper refers to the important applications of tannin, not only in dyeing, but for weighting silks, for tanning skins, for making inks, and as an antiseptic. If tannin serves as a mordant for alkaloïdal colours, it is by reason of its property of forming insoluble compounds with these colours. To prepare the most insoluble compounds or lakes of tannin with the following colours, there are required—

To 4 parts magenta, 5 of tannin and 2 sodium carbonate, and

To 4 parts aniline-violet, 5 parts of tannin and 1 sodium carbonate.

The same proportion holds good for malachite-green:—

For 4 parts methyl-green, 10 of tannin, and 4 sodium carbonate.

For 4 parts methylene-blue, 5 of tannin, and 4 tartar-emetic.

Methylene-blue with five times its weight of tannin forms a soluble compound: finally to precipitate the tannin are required to 5 parts 1 part tartar emetic and 1 sodium carbonate. Tannin, or the astringents containing it, may be condensed on vegetable fibre without the intervention of an intermediary or a mordant. In dyeing, cotton absorbs tannin slowly, and the process cannot be accelerated by heat greater than  $50-60^{\circ}$ : above this limit, the solvent no longer yields

tannin, and the fibre begins to give it up again. This is one of the reasons why preparations in pure tannin require to be dried in hot air, and why they become streaky on drying cylinders heated with steam. Two methods of tanning cotton are known, viz., by dyeing or padding. In the latter case, the solution must be ten times stronger. By dissolving methylene-blue in an excess of tannin, the latter being in greater proportion as the bath is more dilute, it is possible to dye directly a light blue. To obtain a heavy blue, saturate in tannin at 24 grams per litre, dry, fix in iron acetate at  $14^{\circ}$  B., neutralised with 25 grams chalk per litre; wash, dye in methylene-blue, and soap. With iron and astringents, calico printers have compounded colours ever since the rise of this industry. Thus a black may be obtained with 1 litre tragacanth mucilage, 1 litre iron pyrolignite at  $18^{\circ}$  B., 125 grams tartaric acid, and 250 grams tannin. By diluting this colour, greys are obtained rivalling the alizarin colours in fastness. These greys may be dyed with other colouring matters, and preserve their tone on cloth prepared with stannates. Gallic acid greys are purer than tannin greys, but they are wanting in solidity. Since the acquisition of the aniline colours, tissue printers make frequent use of the process of dyeing which consists in turning the mordants into tannates. These mordants, after dunging, are dyed in tannin with addition of gelatin.

D. B.

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## General and Physical Chemistry.

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**Existence of a Dielectrical Polarisation in Electrolytes.** By R. COLLEY (*Ann. Phys. Chem.* [2], 15, 94—111).—There are series of similarly constituted bodies, the extreme members of which are dielectrics and conductors respectively. The experimental researches to which the paper relates were undertaken with a view of determining whether the intermediate members of such series do not exhibit phenomena indicating the simultaneous existence of dielectric and of galvanic polarisation, and the paper describes fully the apparatus and methods employed by the author, whose results show that certain substances do indeed present these phenomena. The investigation supplies a fresh experimental proof of the correctness of the notions propounded by Faraday and by Clerk Maxwell; and dielectrical polarisation, which has nothing in common with galvanic polarisation, is found to exist, not in insulators only, but also in conductors, and this is most notably the case in decomposable conductors. The methods employed in the investigation did not allow of an exact determination of the values of the dielectric constants, but it became evident that those of electrolytically conducting bodies were of the same order of magnitude as those of the true dielectrics. R. R.

**Application of the Telephone to the Estimation of Resistances in Galvanic Circuits and Batteries.** By E. LESS (*Ann. Phys. Chem.* [2], 15, 80—94).—The paper gives the details of the author's experiments on the applicability of the telephone in the estimation of electric resistances under very various conditions. R. R.

**Electrolysis.** By D. TOMMASI (*Compt. rend.*, 94, 1051—1053).—The author has made several experiments, all of which confirm the law that in order that decomposition may take place when a current passes through several electrolytes, it is necessary that the quantity of heat developed by the battery should be equal to the sum of the quantities absorbed by each electrolyte plus the quantity necessary to overcome the total resistance of the electrolytes. By heat produced by the battery is meant that transmissible to the circuit. In many cases in which there is no decomposition when both electrodes are of platinum, decomposition takes place when the positive electrode consists of some oxidisable metal, such as copper or tin. When the current from two Daniell elements is passed through two voltmeters containing water acidulated with sulphuric acid, the positive electrodes being made of silver, the water is decomposed, although, according to the law, no decomposition should take place. This fact affords further confirmation of the author's hypothesis that certain metals have the property of modifying the electrical resistance of certain liquids. The author has also collected a number of facts with regard to the relation which

subsists between the heat produced by a battery and that absorbed by several voltmeters containing water, saline solutions, or fused salts.

C. H. B.

**Thermal Conductivity of Minerals and Rocks.** By J. THOULET (*Compt. rend.*, **94**, 1047—1048).—The author denotes by the term *thermal resistance* the time required for the communication of a certain interval of temperature (in his experiments  $34^{\circ}$ ) from the lower surface of a plate of rock or mineral, 0.01 m. in thickness, and in contact with a source of heat at  $100^{\circ}$ , to the upper surface. This resistance is evidently a function of the coefficient of conductivity. The thermal resistance of glass, iron, and anhydrite was determined by placing plates of these substances from 0.007 m. to 0.015 m. in thickness on a block of iron heated to a temperature which varied between  $100^{\circ}$  and  $160^{\circ}$ , but was constant for the same series of experiments. On these plates were put small quantities of stearin, m. p.  $50^{\circ}$ , and of Carnauba wax, m. p.  $84^{\circ}$ . The time which elapsed between the melting of these two substances was noted, and a curve was constructed having for abscissæ the temperature of the source of heat, and for ordinates the time. The curves thus obtained for the three substances are equilateral hyperbolas. A second series of curves is constructed having for abscissæ the thickness of the plates of the material, and for ordinates those relative to the time-temperature curves previously obtained. The thermal resistance is then given by the length of the ordinate which has for its abscissa the thickness 10, and meets the isothermal for  $100^{\circ}$ . This curve is a non-equilateral hyperbola. The following results were obtained:—

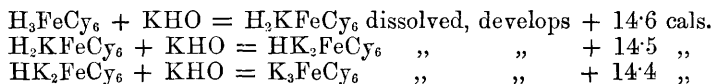
	Thermal resistance.	Coefficient of conductivity.
Glass .....	12.2.4	2.66
Iron (wrought) ....	42.3	10.26
Anhydrite .....	56.4	4.56

C. H. B.

**Hydroferricyanic Acid.** By JOANNIS (*Compt. rend.*, **94**, 449—452, and 531—534).—The author has determined the heat of formation of potassium ferricyanide by means of four reactions: (1) the conversion of potassium ferrocyanide into the ferricyanide by means of bromine; (2) the same change by means of chlorine; (3) the conversion of zinc ferricyanide into ferrocyanide by the action of potassium iodide; (4) the conversion of hydroferrocyanic acid into hydroferricyanic acid by means of bromine, and has obtained, as a mean result, for  $K_3 + Fe + Cy_6 = K_3FeCy_6 + 280.5$  cals.

The methods given in the books for the preparation of hydroferricyanic acid do not yield a pure product. When 1 equivalent of potassium ferricyanide is mixed with 1 equivalent of lead nitrate, a double ferricyanide of lead and potassium is obtained; when more than 3 equivalents of lead nitrate are used for each equivalent of potassium ferricyanide, a double compound of lead ferricyanide and nitrate is formed. With intermediate proportions mixtures of the two double compounds are obtained. On treating the solutions with sulphuric

acid, a mixture of hydroferricyanic and nitric acids is produced, and the brown needles obtained by evaporating the clear liquid are not hydroferricyanic acid, but an alteration product, which gives the reactions for nitroprussides. In order to determine the heat of neutralisation of hydroferricyanic acid, the author measured the heat developed by the decomposition of potassium ferricyanide by sulphuric and tartaric acids respectively, and also that developed by the neutralisation of a mixture of hydroferricyanic acid and hydrobromic acid obtained by the action of bromine on hydroferrocyanic acid. By means of the last reaction he finds that



hydroferricyanic acid is therefore a true tribasic acid.

The following numbers for the heat of neutralisation of the acid by potassium were obtained by the three methods.

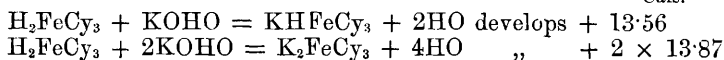
With sulphuric acid	.....	+ 3 × 14·3
,, tartaric	,, .....	+ 3 × 14·4
,, hydroferricyanic acid..		+ 3 × 14·5

From these results combined with those given above, it follows that  $\text{H}_3 + \text{Fe} + \text{Cy}_6 = \text{H}_3\text{FeCy}_6$ , dissolved, develops + 93·6 cal.

C. H. B.

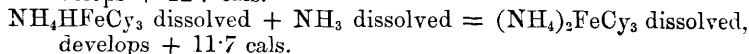
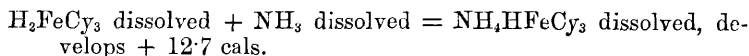
**Heat of Formation of Hydroferrocyanic Acid and of some Ferrocyanides.** By JOANNIS (*Compt. rend.*, **94**, 725–727).—*Hydroferrocyanic acid*,  $\text{H}_2\text{FeCy}_3$ . \*—Heat of solution at  $10^\circ = + 0\cdot2$  cal.

Cals.



From these data, and the heat of formation of potassium ferrocyanide (+ 182·6 cal.) it follows that the heat of formation of hydroferrocyanic acid = + 53·1 cal. solid; + 53·3 cal. dissolved. Berthelot found for the dissolved acid + 53·6 cal.

*Ammonium Ferrocyanide*.—Crystallises with 3HO. Heat of solution at  $14^\circ = - 3\cdot4$  cal.



The heat of formation of  $(\text{NH}_4)_2\text{FeCy}_3 + 3\text{HO}$  from solid acid, gaseous ammonia, and solid water, is therefore + 43·4 cal.

*Barium Ferrocyanide*.—Crystallises with 6HO, and is only slightly soluble in cold water; 1000 parts water dissolve 1 part salt. Heat of solution at  $13\cdot5 = - 5\cdot7$  cal.

\* In this abstract the atomic weights and formulæ given in the original paper are retained, O = 8, &c.

$\text{H}_2\text{FeCy}_3$  dissolved +  $\text{BaO}$  dissolved =  $\text{BaHFeCy}_3$  dissolved +  $\text{HO}$   
develops + 14.58 cal.

$\text{BaHFeCy}_3$  dissolved +  $\text{BaO}$  dissolved =  $\text{Ba}_2\text{FeCy}_3$  dissolved +  $\text{HO}$   
develops + 13.28 cal.

The heat of formation of the salt from anhydrous baryta, anhydrous acid, and solid water = + 57.4 cal.

*Calcium Ferrocyanide*.—Crystallises with  $12\text{HO}$ , and is very soluble in water. Heat of solution at  $10^\circ$  = - 23 cal.

$\text{H}_2\text{FeCy}_3$  dissolved +  $\text{CaO}$  dissolved =  $\text{CaHFeCy}_3$  dissolved +  $\text{HO}$   
develops + 14.2 cal.

$\text{CaHFeCy}_3$  dissolved +  $\text{CaO}$  dissolved =  $\text{Ca}_2\text{FeCy}_3$  dissolved +  $\text{HO}$   
develops + 14.0 cal.

The heat of formation of the salt from calcium oxide, anhydrous acid, and solid water = + 40.1 cal.

From the above numbers it is evident that hydroferrocyanic acid is a true dibasic acid, and closely resembles hydrochloric acid in the amount of heat developed on neutralisation with alkalis and alkaline earths.

C. H. B.

**Influence of Heat on the Molecular Structure of Zinc.** By S. KALISCHER (*Ber.*, 14, 2747—2753).—Rolled zinc when heated at temperatures from  $130$  to  $300^\circ$ , becomes crystalline; this change of structure is accompanied by loss of ring, and the metal may be bent easily; this bending is accompanied by sounds similar to that observed in the case of tin. The crystallisation is well shown by dipping the zinc after heating into a solution of copper sulphate, and is more marked the higher the temperature to which the zinc has been previously heated. The sp. gr. is also altered, being 7.1841, instead of 7.1812 (water at  $0^\circ$  = 1). Its electrical resistance and other physical properties are also influenced by the action of heat. The author proposes to investigate the action of heat on other metals. P. P. B.

**Molecular Structure of Metals.** By S. KALISCHER (*Ber.*, 15, 701—713).—Although most of the metals are known in the crystalline form, yet it is generally held that they have lost their crystalline character when rolled out into foil or wire, although no observations have been made on this point. The author in some former experiments (preceding Abstract) found that non-crystalline zinc-foil becomes crystalline when heated to  $150^\circ$ . Similarly the crystalline structure of cadmium, which is not altogether lost in the process of hammering out, becomes more manifest when the metal is heated to  $200$ — $280^\circ$ , and subsequently etched by copper sulphate solution; the same observation holds good with tin. Iron and copper show traces of crystalline structure when left in contact with nitric or hydrochloric acid, but the best result is obtained when the plates are made the positive electrode for the electrolysis of potassium, ferrous, or copper sulphate or nitrate. Specimens of brass containing 36—66 per cent. of copper, displayed a crystalline structure when made the positive electrode of solutions of copper sulphate or nitrate. Specimens of

pinchbeck were also recognised as crystalline. In the cases mentioned above, the galvanic current as such does not produce the crystalline state, but the solvent power of the electronegative constituent of the electrolyte, for it is observed that metals which do not show any crystalline appearance when corroded by free acids, or solutions of salts, do not show it under the influence of the electric current.

Lead-foil is crystalline; silver-foil becomes crystalline when heated to a red heat, as shown by the action of concentrated nitric acid; gold-foil shows crystalline structure when heated, and subsequently etched by warm aqua regia. The crystalline appearance of platinum, when warmed with aqua regia, has previously been observed by Phipson and Noble, even if not previously heated. German silver shows no crystalline structure when made the electrode of a copper sulphate solution, but the crystalline character becomes manifest when the metal is corroded with dilute nitric acid. No crystalline structure could be recognised in nickel, aluminium, or magnesium cobalt.

From these experiments, it appears that metals whose crystalline structure may be detected when rolled out into foil are also crystalline when cast. The author has accordingly examined bars of copper, brass, steel, bronze, tin, zinc, and cadmium, and has detected by the methods described above a crystalline structure; aluminium and nickel, however, show no crystalline structure.

These facts are of great theoretical importance as regards the difference of electric conductivity of metallic wires, for it has been shown by Siemens and by Matthiessen that the conductivity of wires of silver, copper, platinum, brass, and gold is increased from 1—10 per cent. by heating. From the author's experiments, it follows that this increase of conductivity must be attributed to a change of molecular structure.

The author has examined the conductivity of non-crystalline and crystalline wires of platinum, gold, silver, brass, copper, and zinc, and has confirmed Matthiessen's results. In the case of cadmium, sometimes an increase, sometimes a decrease, and at other times no change was observed in the conductivity; in the case of iron and steel no difference was observable.

These experiments give as result that the *crystalline is the natural structure of most metals, but by mechanical processes some metals lose this structure easily, others with difficulty, and others hardly at all, but assume it again under the influence of heat; and increase of electric conductivity is involved in this change of molecular structure.*

V. H. V.

**Remarks on the Theories of Bergmann and Berthollet.**  
By N. MENSCHUTKIN (*Jour. Russ. Chem. Soc.*, April, 1882, 160—161).  
—The author investigated the action of two different bases on one acid in molecular proportions in a homogeneous system. He finds that either one base is completely displaced by the other, in accordance with Bergmann's views and Berthelot's "principle of maximum of work:" or, that the acid unites partly with each of the bases, in accordance with Berthollet's theory; but that neither of the theories holds good taken by itself. The author is continuing his experiments.  
B. B.



**Atomic Weight of Carbon.** By H. E. ROSCOE (*Compt. rend.*, **94**, 1180).—The author has repeated the determination of the atomic weight of carbon by the method of Dumas and Stas, using Cape diamonds, which contain no trace of hydrogen, but leave a small quantity of ash. As the mean of six experiments he finds that if  $O = 15.96$ ,  $C = 11.97$ .

Dumas points out that if O is taken as 16, then  $C = 12.002$ .

C. H. B.

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## Inorganic Chemistry.

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**Dissociation of Chlorine.** By A. P. SMITH and W. B. LOWE (*Chem. News*, **45**, 226).—If chlorine, dissociated by heat, be passed into a solution of potassium iodide, less iodine should be liberated than would be under normal conditions, and the amount liberated should correspond with the dissociated chlorine. A known volume of chlorine was passed through a glazed porcelain tube heated to  $1030^{\circ}$  into potassium iodide, when less iodine was liberated than when the same volume of chlorine was passed through the cold tube; further experiments with more carefully dried and purified gas showed that 0.01838 gr. Cl at  $7.5^{\circ}$  became 0.01369 gr. Cl at  $1030^{\circ}$ , or as 1:0.744. Mayer found the density at  $1028^{\circ}$  to be 1.89, which is to the vapour-density at  $600^{\circ}$  (2.46) as 0.76:1. E. W. P.

**Vapour-density of Bromine.** By H. JAHN (*Monatsh. Chem.*, **3**, 176—194).—The vapour-density of this element was first determined in 1833 by Mitscherlich, who found it, by Dumas' method, to be 5.54 at  $99.34^{\circ}$  C.; and V. and C. Meyer have lately obtained the value 5.38, both these values agreeing nearly with the number 5.5247 calculated according to Avogadro's law from the atomic weight 79.951 determined by Stas. No exact determinations have however yet been made of the variations in vapour-density of bromine at different temperatures, analogous to those of chlorine which were made some years ago by E. Ludwig; and this deficiency the author of the present paper has endeavoured to supply. Pure bromine was prepared by the method of Stas, the details of which are fully given in the original paper, and the density of its vapour was determined by Bunsen's method. Five series of experiments were made, the mean results of which are as follows:—

	Temp. C.	Density.		Temp. C.	Density.
I .....	102.60°	5.278	IV .....	210.32°	5.546
II .....	131.92	5.635	V .....	227.94	5.5243
III .....	175.58	5.6040			

This last number is very near the value calculated from the atomic weight.

If now these experimental values of the vapour-density of bromine

at different temperatures be inserted in the formula  $D = a + bt$ , and the results calculated by the method of least squares, we find, as the most probable values of the two constants,  $a = 5.8691$  :  $b = -0.00153$ ; and by inserting these values in the above linear formula, we obtain for the densities, numbers agreeing nearly with those found by direct observation: thus—

Temp. C.	Vapour-density.	
	Calc.	Exp.
102.60°	5.7122	5.7280
131.92	5.6673	5.6400
175.58	5.6005	5.6040
210.32	5.5472	5.5460
227.92	5.5204	5.5243

Calculating from these values the vapour-density of bromine for temperatures above its boiling point at intervals of 20°, and making a similar calculation for chlorine from the data furnished by Ludwig's experiments, the author shows that, whereas chlorine at temperatures near its boiling point ( $-33.6^\circ$ ) deviates from its normal vapour-density much less than bromine, the latter, on the other hand, as its temperature is raised, approximates to its normal density much more quickly than chlorine. Chlorine in fact does not attain its normal density till it has been raised  $240^\circ$  above its boiling point, whereas bromine attains that condition at  $160^\circ$  above its own boiling point.

On the vapour-density of iodine at different temperatures no experiments have yet been made analogous to those relating to chlorine and bromine; but the accordant experiments of Victor Meyer and of Crafts and F. Meyer, show that iodine attains its normal vapour-density at temperatures very near its boiling point ( $250^\circ$  according to Stas). Thus Victor Meyer found for the density of iodine-vapour at  $253^\circ$ , the number 8.83, the normal density being 8.78. H. W.

**Activity of Oxygen.** By M. TRAUBE (*Ber.*, 15, 659—675).—In the course of some preliminary observations, the author contrasts the passivity of oxygen under ordinary conditions, with its activity in the presence of animal or vegetable organisms or of finely divided platinum or phosphorus; and alludes to the various theories propounded by De la Rive, Liebig, Schönbein, Brodie, and others, to explain these differences of function.

In the year 1858 the author put forward the view that the activity of oxygen is produced by the presence of substances which possess the property of transferring the oxygen from one compound to another. For example, platinum, according to De la Rive, takes up oxygen, to give it up to other substances present. Similarly ammoniacal solutions of copper salts, indigo-carmine, &c., are deoxidised and decolorised by grape-sugar, but in contact with oxygen resume their original colour, these changes being renewed until all the sugar has been completely oxidised.

In the present communication, the author deals with the formation of hydrogen peroxide in oxidation processes, its chemical structure

and reactions. Schönbein has observed the formation of hydrogen peroxide in many processes of oxidation, and supposed that the oxygen is converted into two modifications, ozone and antozone, the latter of which oxidises the water present to hydrogen peroxide. According to Thénard, hydrogen peroxide is a universal product of the oxidation of the water by the splitting up of the oxygen molecule into active atoms, one of which combines with and is fully retained by the water. This hypothesis the author has experimentally investigated.

If active oxygen were formed by shaking up zinc with atmospheric oxygen and water, an easily oxidisable substance, such as indigo-sulphonic acid, would quickly be oxidised and decolorised; but this is found not to be the case, although hydrogen peroxide is formed; a similar result was obtained on substituting copper for zinc. It is further found that the zinc, when shaken with air and ammonia, forms hydrogen peroxide, but were the hypothetical active oxygen present, the ammonia would be oxidised to ammonium nitrite or nitrate; but no traces of these substances could be detected. Conversely, the author examined whether oxygen is converted into the active form in the reduction of potassium nitrate by zinc, and found that the reduction to nitrite or ammonia proceeds as readily in the presence as in the absence of air; the ammonia formed in the reduction is not oxidised to ammonium nitrite and nitrate, even when the reacting substances are shaken up with a large excess of air, and although the presence of hydrogen peroxide could be detected. Hence the hypothesis that the hydrogen peroxide is formed by the splitting up of the molecule of oxygen is not confirmed by experiment, and the author puts forward the view that it is not the oxygen, but the more easily decomposed water molecule, which is thus split up; and that hydrogen peroxide is not oxidised water but reduced oxygen. In confirmation of this view the author mentions the fact that the alkali-metals, which remain unchanged in presence of dry oxygen, decompose water readily. Thus the formation of hydrogen peroxide, by the action of air and water on zinc, can be written thus:  $\text{Zn} + \text{O} \mid \text{HH} + \text{O.O} \mid = \text{ZnO} + \text{H.O.OH}$  and

$\text{ZnO} + \text{H}_2\text{O} = \text{Zn(OH)}_2$ . If these equations represent the change correctly, then for every molecule of the metallic hydroxide a molecule of hydrogen peroxide should be formed; and this relation Schönbein has established in the case of lead at the beginning of the reaction; but afterwards the secondary change,  $\text{Zn} + \text{H}_2\text{O}_2 = \text{Zn(OH)}_2$ , takes place. Similarly the formation of hydrogen peroxide by the action of acids on the metallic peroxides, does not involve the oxidation of water, but the interchange of the metal with the hydrogen of the acid. The above hypothesis explains the reduction of potassium nitrate by zinc in presence of water, the change being represented thus:  $\text{Zn} + 2\text{OH}_2 + \text{O.NO}_2\text{K} = \text{Zn(OH)}_2 + \text{H}_2\text{O} + \text{KNO}_2$ ; and is precisely analogous to the action of zinc on water in presence of air, with this exception, that a molecule of water is formed instead of a molecule of hydrogen peroxide. The reduction of nitrates by zinc or lead cannot be said to be due to nascent hydrogen; since these metals do not liberate hydrogen from water in the absence of the nitrate. Nor again can the formation of nitric oxide by the action of copper on nitric

acid, be considered due to the reduction of the nitric acid by nascent hydrogen, but to the decomposition of water by the two opposing affinities of the copper for the hydroxyl, and the oxygen of the nitric acid for the hydrogen of the water, thus:  $2\text{HNO}_3 + 3\text{Cu} + 2\text{H}_2\text{O} = 2\text{NO} + 3\text{Cu}(\text{OH})_2$  and  $3\text{Cu}(\text{OH})_2 + 6\text{HNO}_3 = 3\text{Cu}(\text{NO}_3)_2 + 6\text{H}_2\text{O}$ .

The theory here put forward is based on the supposition, that those substances which by their oxidation form hydrogen peroxide must possess reducing properties, as the hydrogen peroxide is formed by a reducing action. This is confirmed by observation; zinc and lead give hydrogen peroxide, reduce nitrates to nitrites, and decolorise indigo-carmin. Copper gives no hydrogen peroxide, and does not reduce neutral solutions of nitrates.

It is well known that hydrogen peroxide possesses both an oxidising and a reducing action, and it has hitherto been supposed that by the contact of hydrogen peroxide with substances which easily give off oxygen, both the former and the latter are reduced; but in reality only the latter are reduced, the hydrogen peroxide, or rather its hydrogen-atoms, are oxidised and its oxygen liberated as such.

The view that hydrogen peroxide is not oxidised water was put forward by Weltzein (*Annalen*, **115**, 121, and **138**, 129), but seems to have remained unnoticed by chemists.

The evolution of heat in the decomposition of hydrogen peroxide by platinum militates against the hypothesis that hydrogen peroxide is oxidised water; this evolution arises from a combustion of the hydrogen and oxygen within the molecule of hydrogen peroxide; for were hydrogen peroxide produced by the oxidation of preformed water, the decomposition into its two constituents would be accompanied by an absorption and not an evolution of heat.

V. H. V.

**Oxidation by Ozone.** By MAILFERT (*Compt. rend.*, **94**, 1186—1187).—When perfectly dry ozone acts on dry sulphur, sulphurous anhydride is the sole product, but in presence of water, sulphuric acid only is formed. If an alkali is present a sulphate is produced. With selenium and tellurium in presence of water, selenic and telluric acids are the only products; selenious and tellurous acids are not formed. Most, if not all sulphides are attacked more or less rapidly by ozone, with formation, in some cases, of a sulphate, in others, of sulphuric acid and a peroxide. The sulphides of copper, antimony, zinc, cadmium, the alkali-metals, and the alkaline-earth-metals, yield sulphates. Nickel and cobalt sulphides are first converted into sulphates, then a portion of the sulphuric acid is set free and a peroxide formed. Gold sulphide yields metallic gold and sulphuric acid. Platinum, bismuth, and silver sulphides also yield free sulphuric acid. The sulphides of mercury are only very slowly attacked. Prolonged action of ozone on lead, manganese, and palladium sulphides, converts them entirely into peroxides, sulphuric acid being set free. In the case of manganese, some permanganic acid is also formed. The corresponding sulphates are decomposed by ozone in a similar manner.

Methane and ethylene yield carbonic, formic, and acetic acids. Acetylene yields carbonic and formic, but no acetic acid. Amylene yields carbonic, butyric, and valeric acids; formic and acetic acids if

produced at all, are formed only in very small quantity. Benzene and toluene yield carbonic, formic, and acetic acids, and probably other acids of the fatty series. In addition, benzene yields a deep brown solid, and toluene a deep brown syrupy liquid. In the case of benzene, some oxalic acid is formed, and if the oxidation takes place in presence of nitrogen, a small quantity of nitrobenzene is also produced.

C. H. B.

**Density and Chlorination of Sea-water taken by the "Travailleur" in 1881.** By B. DE LA GRYE (*Compt. rend.*, **94**, 1063—1066).—The following results (p. 799) were obtained; the density in the sixth column is calculated from the amount of chlorine by multiplying by .00167, and adding the number thus obtained to the constant 0.9944. If the density at 20° is required, the factor is 0.0016.

It is evident that the density and salinity gradually increase on passing from the ocean to the Mediterranean. The surface water is less dense and less saline than that below, and, generally, the increase varies as the depth. In order to maintain oceanic equilibrium, the lighter water must stand at a higher level, and the author has calculated from the density at different depths in different localities, the sea-level in those localities, and has obtained numbers closely agreeing with those which Bourdaloue obtained by levelling.

C. H. B.

**Formation of Hydrogen Dioxide by the Oxidation of Terpenes.** By W. RADULOWITSCH (*Journ. Russ. Chem. Soc.*, April, 1882, 176—190).—The author has studied the reactions and other properties of "turpentine-water" which is obtained by shaking water with turpentine in the presence of air; and he shows that it does not differ in its properties from a solution of hydrogen dioxide. The quantity of the latter seems to increase if the action takes place at a higher temperature (about 90°). The author proves the presence of hydrogen dioxide in this "turpentine-water" by its ordinary reactions, and estimates its quantity either colorimetrically from the intensity of the blue colour of the chromium peroxide formed, or by measuring the volume of oxygen which is evolved when hydrogen peroxide is decomposed by platinum black, blood, or lead dioxide, this being a quick mode of its estimation in "turpentine-water" largely used for disinfecting purposes.

B. B.

NOTE.—The preparation of a dilute solution of hydrogen peroxide in this way, and its use as a disinfectant, was long ago practically carried out by C. T. Kingzett, to whose paper Radulowitsch refers, remarking that his own results were published in Russian in 1869.—C. E. G.

**Amount of Ammonia Absorbed by Hydrochloric Acid from the Air.** By R. HEINRICH (*Biol. Centr.*, 1882, 226—228).—The amount which hydrochloric acid exposed in pans can absorb from the air is at the maximum during June—August, and in the experiments 9.766 mgrms. N were absorbed by a surface of 78.5 sq. cm. The minimum occurs in December—February (2.912 mgrms. N). Schlösing calculates from summer experiments that 62 kilos. N per hectare are absorbed annually, but this is erroneous, as the quantity would have been considerably reduced if experiments had been made in winter; this new

Date.	Position.	Depth in metres.	Density at 15°.	Chlorine per litre.	Density calculated.	Error.
July 5 .....	42° 52' N., 2° 58' 30" E. ..	{ Surface 600 1,000	1·02875 1·02926 1·02933	20·93 21·27 21·40	1·0293 1·0299 1·0301	+ 0·0005 + 0·0006 + 0·0004
July 7 .....	Before Nice .....	{ 300 600	1·02912 1·02935	21·00 21·04	1·0295 1·0296	+ 0·0004 —
July 12 .....	43° 15' N., 5° 1' E. ....	{ 600 1,200 1,800 2,400	1·02964 1·02948 1·02972 1·02896	21·09 20·99 21·33 20·85	1·0296 1·0294 1·0300 1·0292	— — 0·0001 + 0·0003 + 0·0003
July 26 .....	33° 30' N., 5° 12' W. ....	{ 200 400	1·02855 1·02894	20·65 20·85	1·0288 1·0292	+ 0·0003 + 0·0003
August 7 .....	39° 35' N., 12° 4' 30" W. .	1,500	1·02795	20·19	1·0281	+ 0·0002
August 17 .....	44° 48' 30" N., 7° 1' 30" W.	{ Surface 500 1,000 1,500 2,000	1·02718 1·02743 1·02752 1·02752 1·02756	19·85 19·83 19·92 19·90 19·87	1·0276 1·0276 1·0277 1·0277 1·0276	+ 0·0004 + 0·0002 + 0·0002 + 0·0002 —

set indicates 30.6 kilos. N as the amount of ammonia per hectare which can be absorbed by the soil. Pure water seems incapable of absorbing ammonia from the air.

E. W. P.

**Action of Gaseous Ammonia on Ammonium Nitrate.** By RAOULT (*Compt. rend.*, **94**, 1117—1118).—By measuring the tensions of dissociation, Troost has shown that the liquid obtained independently by Divers and the author by the action of ammonia gas on ammonium nitrate, contains the definite compound,  $2(\text{NH}_4\text{NO}_3), 3\text{NH}_3$ . In order to dispense with the special apparatus required for measuring the tensions, the author adopted the following method, which is applicable in similar cases. The substance is heated at gradually increasing temperatures, and weighed from time to time. If it is a definite compound, it experiences no decomposition so long as the temperature is below that at which its tension of dissociation is equal to the atmospheric pressure. As soon, however, as this point is passed, the compound rapidly loses a notable quantity of gas, and suddenly loses weight. In cases in which the gas is simply condensed or dissolved, the loss of weight is regular and continuous. The following results were obtained with ammonium nitrate saturated with ammonia gas at 745 mm. pressure.

Temperature.	Weight of $\text{NH}_3$ gas combined with 100 grams of ammonium nitrate.
0°	48.1
6	42.0
12	32.8
18	32.0
24	28.0
30	18.0

The weight of ammonia united with the ammonium nitrate diminishes rapidly from 0° to 12°, is constant from 12° to 18°, but diminishes rapidly between 18° and 30°. The liquid evidently contains a definite compound formed by the union of 32.4 parts ammonia with 100 parts ammonium nitrate. This corresponds with the formula



identical with that found by Troost. It is also evident that this compound can dissolve considerable quantities of ammonia gas at low temperatures. Ammonium nitrate, on the other hand, is not sensibly soluble in the definite compound. To convert the liquid saturated with ammonia at a low temperature into the definite compound, it is only necessary to agitate with finely powdered ammonium nitrate until no more is dissolved.

C. H. B.

**Pernitric Acid.** By P. HAUTEFEUILLE and J. CHAPPUIS (*Compt. rend.*, **94**, 1111—1114).—The authors have previously shown that the ozone produced by the action of the electric discharge on dry air is mixed with pernitric acid. The formation of the latter compound is limited, like that of ozone, and the maximum corresponding with a given temperature may be determined from the diminution of pres-



sure. Moreover, when the maximum is reached, the pernitric acid undergoes periodical retrogradation and re-formation as already observed in the case of ozone (this vol., p. 688). This decomposition of the pernitric acid into oxygen and hyponitric acid also causes the decomposition of the admixed ozone, even at pressures above 100 mm., although ozone unmixed with pernitric acid does not undergo retrogradation at these pressures. This result is probably due to the development of heat accompanying the decomposition of the pernitric acid. At ordinary pressures in presence of certain proportions of hyponitric acid, the ozone and pernitric acid are not re-formed, but under low pressures they are again produced. The amount of pernitric acid formed depends more on the temperature than on the relative proportions of oxygen and nitrogen; and to obtain a good yield the operation should be conducted at a low temperature. The maximum quantity produced at 15° under a pressure of 600 mm. is about 30 per cent. by weight. The formation and decomposition of the pernitric acid may be traced with the aid of the spectroscope.

C. H. B.

### **Formation of Hydrogen Sulphide from Sulphur and Water.**

By J. BOEHM (*Monatsh. Chem.*, **3**, 224—227).—The author, after referring to observations made by himself and others on the formation of hydrogen sulphide by the action of water on vulcanised caoutchouc and other organic substances containing sulphur, proceeds to examine the conditions most favourable to the formation of this gas by the action of water on free sulphur.

When flowers of sulphur are kneaded in ordinary water, the floating portions removed, and the immersed portions left in an open vessel covered with only a small quantity of water, sulphuric acid is produced, whereas if the flowers of sulphur are kept in spring-water, and the air is excluded, hydrogen sulphide is formed after a short time. Flowers of sulphur which have been kept for a month or longer in well-water, daily changed, immediately produce hydrogen sulphide, and, after a few days, the water, if its volume does not greatly exceed that of the flowers of sulphur, gives with potassic lead-solution a black precipitate, and with barium chloride a moderate turbidity. In sealed tubes, with flowers of sulphur not very well adapted for the production of hydrogen sulphide, the formation of the gas is permanently hindered by the presence of air, even in small quantity. The same effect is produced by any acid or by phenol; carbon bisulphide prevents the action only when the flowers of sulphur have been well mixed with a few drops of it. Flowers of sulphur thus treated, and then freed from the admixed substance, also those which have been boiled or frozen for some days, do not recover the power of immediately producing hydrogen sulphide till they have been digested for some time in spring-water, daily renewed.

In distilled water, no hydrogen sulphide is evolved, and even flowers of sulphur highly capable of generating this gas, lose the power of immediately producing it, even in spring-water, if they have been washed with pure water and kept for some time. In distilled water mixed with a little chalk, much less hydrogen sulphide is formed than

under similar conditions in spring-water, and a large quantity of chalk prevents the formation of the gas, even under circumstances otherwise favourable. The same is true in a still higher degree for gypsum, and for a considerable quantity of charcoal-powder freed from air by boiling. In the latter case the liquid, which in most cases is faintly alkaline, is strongly clouded by barium chloride.

Hydrogen sulphide is also formed on boiling sulphur in water. Well-water thus treated becomes blue-green, and this colour is produced in like manner in distilled water after addition of chalk. After gradual decomposition of the carbonate, whereby thiosulphate is formed, also on cooling, the liquid becomes yellowish or colourless. When sulphur is boiled with water in a flask fitted with an upright tube, the sides of the flask become coated with crystalline sulphur, and hydrogen sulphide is given off. The decomposition of this compound, with separation of crystalline sulphur, is effected, as is well known, only by sulphurous acid, according to the equation  $2\text{H}_2\text{S} + \text{SO}_2 = 2\text{H}_2\text{O} + 3\text{S}$ , which on the other hand doubtless represents the formation of the hydrogen sulphide. In acidulated water, no hydrogen sulphide is formed. In sealed tubes containing air, also, no hydrogen sulphide is produced from non-floating flowers of sulphur, even after prolonged boiling; but if they also contain chalk, the gas appears after the oxygen of the air has been consumed in the formation of sulphate.

Carbolic acid does not prevent the formation of hydrogen sulphide in boiling water, which takes place, although in comparatively small quantity, at a temperature of  $150^\circ$  or upwards, even in tubes containing air, and in acid liquids.

The quantity of hydrogen sulphide formed, either at ordinary or at higher temperatures, not only from sulphur and water, but also from livers of sulphur, is limited, the presence of a certain quantity of this gas putting a stop to its further evolution.

When flowers of sulphur, in a condition well adapted for the formation of hydrogen sulphide, are kept for some time in spring-water saturated with the same gas, they lose the power of inducing its immediate formation at ordinary temperatures.

The lower sulphides of the alkali-metals and alkaline earth-metals yield hydrogen sulphide only at boiling heat. With pyrites, galena, and zinc-blende, this takes place when they are heated with water for some time in the form of fine powder at  $150$ — $200^\circ$ , the liquid then becoming alkaline, and giving a strong turbidity with barium chloride. Out of four tubes freed from air by boiling and containing galena, two, after ten days' heating, were found to contain a red powder (? minium).

Hydrogen sulphide is known to be formed when hydrogen gas is passed into boiling sulphur. The same result is likewise obtained when floating flowers of sulphur are boiled with distilled water in an atmosphere of hydrogen. On opening the tubes under mercury, a considerable contraction of the still unaltered gas takes place, which is not the case in a similar experiment with flowers of sulphur and ordinary water. In this case, the gas required to put a limit to the process is produced by decomposition of the water. The

contraction is a consequence of the absorption of the gas formed at the expense of the hydrogen.  
H. W.

**Behaviour of Iodine with Sulphuric Anhydride and with the Hydrates of Sulphuric Acid.** By R. WEBER (*J. pr. Chem.* [2], **25**, 224—231).—Bussy (*Annalen* [2], **26**, 419) states that iodine and sulphuric anhydride combine and form a blue-green liquid. Wach (Schweigg, *Journ. Phys. Chem.*, **50**, 37) describes three different compounds of iodine and sulphuric anhydride, one (brown) containing the most iodine; one (green) containing the least, and an intermediate one of a blue colour. On heating the blue variety, it is converted into the brown with loss of anhydride. Fischer (*Pogg. Ann.*, **16**, 121) suggests that of these three only the brown one is stable, and the blue and the green compounds have simply an ephemeral existence.

The author treats pure dry iodine with excess of pure liquid sulphuric anhydride. The experiment is conducted in a V-tube, the end being sealed up after the introduction of the (weighed) iodine. Combination takes place with slight development of heat; a dark green-brown viscid liquid is formed which sinks below the unattacked anhydride (which is quite colourless if no moisture is present; if, on the other hand, some trace of water is present, the mixture is either blue or green); no more anhydride is now taken up, even if the tube is heated to the boiling point of the anhydride. Most of the excess of anhydride can be poured off, and the rest is distilled off by carefully warming. The product is not miscible with sulphuric anhydride; it, however, takes up iodine. It fumes on exposure to the air; crystallises, but not so readily as ordinary anhydride, and, on warming, fuses again easily. When heated to the boiling point of sulphuric anhydride, it parts with some of the latter. From a quantitative experiment and several estimations of iodine in this body, it is shown to contain  $I_2 \cdot 6SO_3$ . When the substance is digested at 95—100° for an hour, a body,  $I_2 \cdot 2SO_3$ , is formed. At ordinary temperatures, it is thick and viscid, but on warming it becomes mobile. It is of a brown colour, and only transparent in thin layers. It fumes in the air, and is decomposed by water with violence, iodine separating out, and sulphuric acid going into solution. No iodine is evolved on heating to 106°. If this substance is heated at 170—175° for one hour it loses anhydride, and the compound  $I_2 \cdot SO_3$  is obtained. This is solid at ordinary temperatures and resembles iodine in appearance. It is decomposed by water, but not so violently as the other compounds. At 160—170° it is slightly volatile, and at higher temperatures it distils with partial decomposition. The author suggests that this compound is too stable to be a mere solution of iodine. Neither of these substances answers to those described by Wach or Fischer, which are really hydrated bodies.

Iodine dissolves in sulphuric anhydride containing only a very little hydrate with a blue colour, and the product can be crystallised. With acid containing less than 94.68 per cent.  $SO_3$ , an emerald-green crystalline product is obtained soluble in the acid. The purity of the colour diminishes as the acid is diluted, and a brown colour is produced with 91.40 per cent. acid. Ordinary fuming sulphuric acid

dissolves iodine with brown colour, and, provided there is not too much iodine present the solution will turn green when heated. Iodine is only slightly taken up by ordinary sulphuric acid. By adding iodine to the blue or green varieties, they ultimately become brown. An analysis of the blue body points to the composition  $2(4\text{SO}_3, \text{H}_2\text{O}), \text{I}_2$ , probably  $6\text{SO}_3, \text{I}_2 + 2(\text{SO}_4\text{H}_2)$ .  
D. A. L.

**Behaviour of Tellurium with Sulphuric Anhydride and with Sulphuric Acid.** By R. WEBER (*J. pr. Chem.*, **25**, 218—231).—Müller and Reichenstein observed that tellurium dissolved in concentrated sulphuric acid with an amethyst-red coloration. Klaproth showed further, that this coloration disappeared on warming, with formation of a white oxidised precipitate, and on diluting the acid finely divided tellurium separated. Magnus suggested that the tellurium was simply dissolved by the acid in the same way as sulphur is, and that oxidation did not take place until the liquid became decolorised, as for example by standing in moist air, when tellurous acid is formed. Fischer, on the other hand, supposes that oxidation does take place, and that the product dissolves in the acid, and is decomposed on diluting with water. All the tellurium, however, is not separated, for an appreciable amount is retained as oxide by the dilute acid.

*Sulphuric Anhydride and Tellurium.*—Finely powdered tellurium is added in small quantities at a time to perfectly pure sulphuric anhydride (solidifying at  $14.8^\circ$ ), the temperature being kept at  $30\text{--}35^\circ$ ; at lower temperatures the mass solidifies, at higher decomposes; at the end of the reaction the excess of anhydride is separated from the amethyst-red viscid product by pouring off and pressing with a glass rod. It is very unstable and decomposes at ordinary temperatures, even in sealed tubes, tellurium separating with evolution of sulphurous acid. When it is heated on the water-bath, a violent evolution of sulphurous acid takes place, and a grey residue of tellurium and tellurous acid remains behind. Similar products are formed when it is decomposed by moisture. It is not soluble in sulphuric anhydride, but is mechanically miscible with an excess, and dissolves in Nordhausen and concentrated sulphuric acid with the characteristic amethyst-red colour. The results of analysis led to the formula  $\text{TeSO}_3$ . It is analogous to the sulphur and selenium compounds,  $\text{S}_2\text{O}_3$  and  $\text{SeSO}_3$ , already described by the author, and hence completes the series of compounds which the sulphur-group of elements form with sulphuric anhydride. All three dissolve in very concentrated sulphuric acid rich in sulphuric anhydride, the sulphur compound with a lapis-lazuli blue, the selenium compound with an emerald-green, and the tellurium with an amethyst-red coloration.

When isolated they are all very unstable; their order of stability is—selenium compound the most, tellurium compound the next, and sulphur compound the least.

With ordinary concentrated sulphuric acid, the blue colour of the  $\text{S}_2\text{SO}_3$  solution changes to yellow-brown, whilst the  $\text{TeSO}_3$  and  $\text{SeSO}_3$  red and green are unaltered. The green colour is, however, destroyed by diluting with a quantity of water equal to half that already con-

tained in the acid; and the red solution requires dilution with a bulk of water equal to that already present in the acid before the colour disappears.

The red coloration observed by Müller and v. Reichenstein, and the reactions, &c., described by the other authors above referred to, are evidently due to the formation of the body  $\text{TeSO}_3$ , and its subsequent solution or decomposition.

D. A. L.

### Action of Hydrogen Sulphide on Nickel Sulphate Solution.

By H. BAUBIGNY (*Compt. rend.*, **94**, 1183—1186).—When hydrogen sulphide is passed into a *neutral* solution of nickel sulphate at ordinary temperatures, about 90 per cent. of the nickel is thrown down as sulphide. The amount precipitated is independent of the concentration of the solution, and of the degree of saturation with hydrogen sulphide, but depends on the duration of the experiment. The precipitation is also affected by the relative quantity of acid and metal, and the addition of an amount of free sulphuric acid equal to one-fourth the quantity of acid in the salt prevents the formation of nickel sulphide.

In the case of zinc sulphate, the precipitation of zinc sulphide is a function of the relative acidity of the solution, and not of the relation between the weights of acid and metal. By sufficiently diluting the solution, all the zinc can be thrown down as sulphide.

C. H. B.

**Hard Bronze of the Ancients.** By E. REYER (*J. pr. Chem.* [2], **25**, 258—262).—After some remarks as to the method probably employed by the ancients in making bronze, the author publishes the following analyses by Luwig:—

I. Fragment of an axe from Maiersdorf. The metal is thick, tenacious, bright yellow. Hardness 5.

II. Axe from Limburg. It is reddish golden-yellow, solid and tenacious, and is hardly scratched by felspar.

III. Fragment of a sword from Steier. The metal is reddish-yellow, solid and tenacious, as the marks of cuts show. It is not easily scratched by quartz.

IV. Chisel from Peschiera. It is deep yellow, like all others found in the same locality, and laid bare by water; it contains a trace of cobalt. Hardness 5.

Neither lead nor zinc was found in any of the specimens.

	Cu.	Sn.	Ni.	Fe.	P.
I.	87.25	13.08	0.38	trace	0.250
II.	83.65	15.99	0.63	trace	0.054
III.	85.05	14.38	trace	trace	0.106
IV.	88.06	11.76	trace	trace	0.027

D. A. L.

*Note.*—In the various specimens of ancient bronze examined by Flight (this Journal, **41**, 142 and 145) lead is generally present.

**Decomposition of Lead Salts by Alkalis.** By A. DITTE (*Compt. rend.*, **94**, 1181—1182).—If lead chloride is suspended in

water, and solution of potassium hydroxide added little by little with continual agitation, the alkalinity disappears up to a certain point, at which the lead chloride is converted into a curdy mass of white transparent needles of the composition  $\text{PbCl}_2, 2\text{PbO}$ . When this compound is suspended in water, and potassium hydroxide added, it undergoes but little decomposition until the degree of concentration of the alkaline solution reaches a certain point, when the oxychloride is rapidly converted into grey anhydrous oxide.

If lead hydroxide is treated with potassium chloride at ordinary temperatures, the liquid becomes alkaline, lead oxychloride and potassium hydroxide being formed. This change goes on until the quantity of alkali present reaches a certain limit, when two changes become possible, viz., the decomposition of the lead oxychloride, with production of potassium chloride and lead oxide, and the conversion of the oxide into oxychloride with formation of potassium hydroxide. A condition of equilibrium is established between the potassium chloride and hydroxide and the lead oxychloride and oxide, the relative proportions of the different substances varying with the temperature. The lead oxychloride formed in this way is slowly coloured deep brown on the surface when exposed to the action of light. Potassium hydroxide decomposes the brown compound, forming lead oxide.

Lead bromide and iodide behave in a similar manner with alkalis. It is also known that lead nitrate gives with ammonia a series of basic nitrates. When potassium hydroxide in slight excess is added to lead nitrate, the compound  $\text{N}_2\text{O}_5, 6\text{PbO}$ , is precipitated. It is decomposed by more concentrated solutions of the alkali, yielding the anhydrous oxide.

C. H. B.

### Reaction of Mercuric Iodide with Sodium Thiosulphate.

By J. M. EDER and G. ULM (*Monatsh. Chem.*, **3**, 197—204).—I. Mercuric iodide dissolves in aqueous sodium thiosulphate, forming a clear colourless liquid, which contains 1 mol.  $\text{HgI}_2$  to 2 mol.  $\text{Na}_2\text{S}_2\text{O}_3$ , or 1 pt. by weight of the iodide to 1.09 of the crystalline thiosulphate.

II. On leaving a cold saturated solution of the two salts to evaporate in a vacuum over sulphuric acid, sulphurous oxide is given off, and a yellow precipitate of mercurous iodide is formed, which quickly turns green, and subsequently becomes mixed with sulphur and mercuric sulphide. On evaporating it to dryness, mercuric sulphide and sodium iodide are formed, a reaction which has been utilised for analytical purposes.

III. The solution is not clouded by ammonia, ammonium carbonate, potassium hydroxide, potassium ferrocyanide or ferricyanide, but alcohol added to the concentrated solution throws down an oily precipitate consisting of sodio-mercuric thiosulphate,  $\text{HgS}_2\text{O}_3, 2\text{Na}_2\text{S}_2\text{O}_3$ , contaminated with excess of the sodium salt, whilst sodium thiosulphate and sodio-mercuric iodide remain in solution:



From a solution of mercuric iodide in potassium thiosulphate, alcohol throws down silky needles of the potassio-mercuric thiosulphate described by Rammelsberg.

IV. The solution of mercuric iodide in sodium thiosulphate decomposes, with or without contact of air, in a few weeks at ordinary temperatures, in a few hours on heating, with evolution of sulphurous oxide, and deposition of a precipitate, yellowish-red if formed in the dark, blackish in the light, and consisting of variable quantities of mercurous iodide (very sensitive to light), mercuric sulphide, and free sulphur. If the solution contains excess of sodium thiosulphate, sulphurous oxide is likewise evolved, and a cinnabar-red precipitate is formed, which contains no free sulphur, inasmuch as sulphur is soluble in sodium thiosulphate.

V. A solution of potassio-mercuric iodide,  $\text{HgI}_2 \cdot 2\text{KI}$ , mixed with sodium thiosulphate yields, after prolonged heating at  $80^\circ$ , a black bulky precipitate containing 14.06 per cent.  $\text{Hg}_2\text{I}_2$  and 67.99  $\text{HgS}$ . The black colour of the precipitate is due to decomposition of the mercurous iodide by potassium iodide, which takes place even without the presence of sodium thiosulphate. The explanation of the process is, therefore, that the potassio-mercuric iodide reacts with the thiosulphate in the same manner as mercuric iodide itself, the resulting mercurous iodide being then acted upon in the manner above mentioned.

VI. The composition of the blackish and yellow precipitates separated from the solution of mercuric iodide in sodium thiosulphate in the light and in the dark respectively (IV) is:—

	In the light.	In the dark.
Mercuric iodide.....	61.10 p. c.	67.54 p. c.
Mercuric sulphide....	24.19 „	27.44 „
Free sulphur.....	14.44 „	5.92 „

The larger proportion of free sulphur deposited on exposure to light is due to the fact that sodium thiosulphate is itself decomposed by light, with separation of sulphur.

VII. A dilute solution of mercuric iodide in sodium thiosulphate acts on finely divided silver (recently precipitated from the nitrate by ferrous sulphate), turning it black, and forming a mixture of mercurous and argentic iodides, part of the latter being, however, dissolved by the thiosulphate. A strong solution of the thiosulphate dissolves out all the silver iodide and part of the mercurous iodide, leaving a dark-coloured mercury-compound.

VIII. The above-described reactions of a solution of mercuric iodide in sodium thiosulphate lead to the inference that a double salt,  $\text{HgI}_2 \cdot 2\text{Na}_2\text{S}_2\text{O}_3$ , is formed, analogous to Kessler's  $\text{Hg}(\text{CN})_2 \cdot 2\text{Na}_2\text{SO}_3$ , a view which is in accordance with the solubility-determination (I). On the other hand, it might be supposed, as already observed, that the double thiosulphate,  $\text{HgS}_2\text{O}_3 \cdot 2\text{Na}_2\text{S}_2\text{O}_3$ , is produced, together with  $\text{HgI}_2 \cdot 2\text{NaI}$ , separable by alcohol (III). If, however, this sodio-mercuric thiosulphate were contained in the solution, the latter could not be kept unaltered for several days; for the double salt in question decomposes soon after its formation, with separation of mercuric sulphide, and consequently the precipitate which gradually forms could not contain mercurous iodide, inasmuch as a solution of sodio-mercuric thiosulphate mixed with potassium iodide, after it has begun to decompose, does not yield a precipitate containing iodine.

Moreover, the last-mentioned double salt (which is stable only in alkaline solution) does not act on silver, or form mercurous oxide, and consequently a mixture of sodio-mercuric thiosulphate and sodio-mercuric iodide could not exhibit the reaction described in IV. The formation of a double salt of mercuric iodide with sodium thiosulphate appears therefore to be demonstrated by the preceding reactions.

H. W.

**Some Reactions of Stannous Salts.** By A. DITTE (*Compt. rend.*, 94, 1114—1117).—Soluble silver salts form with soluble stannous salts, characteristic, highly-coloured precipitates, the composition of which varies with the relative proportions of the reacting bodies. When silver nitrate is added to an excess of stannous nitrate, a white precipitate is produced, which when dry forms a grey powder readily soluble in dilute nitric acid, insoluble in ammonia, but turned deep red by a trace of this reagent. If the white precipitate is left in the original liquid, it becomes red after some time. When suspended in a large quantity of water, it is converted into a deep red powder, which, when dried in a vacuum, is insoluble in ammonia, but soluble in dilute nitric acid. This red compound is silver metastannate,  $5\text{SnO}_2, \text{Ag}_2\text{O}$ . If slowly formed in the original liquid, it contains  $7\text{H}_2\text{O}$ , if formed by suspension in water,  $3\text{H}_2\text{O}$ . Dried at  $80^\circ$ , it has a deep blue-black colour. When heated, it loses water and detonates, with development of heat and light. This detonation is transmitted along a train of the compound, as in the case of gunpowder. The anhydrous metastannate is insoluble in dilute acids, but warm concentrated nitric acid dissolves out silver, leaving metastannic acid.

When the stannous salt is added to an excess of silver nitrate, a white precipitate is formed which rapidly becomes red, and eventually deep red, almost black. The filtrate is colourless, but after a short time deposits the same precipitate. Several hours are required for complete precipitation. The dark red precipitate is well washed and dried in a vacuum. It is silver stannate,  $\text{SnO}_2, \text{Ag}_2\text{O} + 2\text{H}_2\text{O}$ , soluble in dilute nitric acid, but insoluble in ammonia. When heated, it loses water without detonation or incandescence, and becomes insoluble in dilute acids.

When very dilute stannous nitrate in slight excess is added little by little to silver nitrate, a deep reddish-purple precipitate is deposited after some time. This dissolves in nitric acid, forming a clear yellow solution, and also in ammonia, forming an intensely red liquid. When exposed to the air, the dilute ammoniacal solution is completely decolorised after some time, but if it contains a moderate quantity of the silver salt, it deposits on evaporation a purple precipitate having all the properties of the original substance. When this precipitate is washed and dried, either in a vacuum or at  $30^\circ$ , it forms small friable masses with a vitreous fracture, entirely soluble in cold dilute ammonia. In the formation of this compound,  $5\text{SnO}_2, \text{Ag}_4\text{O}, 2(\text{SnO}_2, \text{Ag}_2\text{O}) + n\text{H}_2\text{O}$ , a portion of the stannous salt is oxidised to stannic acid, and a portion of the silver salt is reduced to suboxide. The compound loses water when heated, and becomes insoluble in ammonia.

Platinum chloride and palladium nitrate behave in a similar manner.



Palladium nitrate, added to an excess of stannous salt, forms very deep brown palladium metastannate,  $5\text{SnO}_2, \text{PdO} + 4\text{H}_2\text{O}$ , insoluble in ammonia, but soluble in hydrochloric acid, forming a deep brown solution, and in nitric acid forming a reddish-yellow solution. Platinum chloride under similar conditions, forms a blood-red metastannate,  $5\text{SnO}_2, \text{PtO} + 4\text{H}_2\text{O}$ , insoluble in ammonia, but soluble in hydrochloric acid, forming a beautiful red solution, and in nitric acid forming a yellowish solution. Both these compounds when heated lose their water with detonation and incandescence, and become insoluble in dilute acids. If the palladium or platinum salt is in excess, highly coloured stannates soluble in dilute acids, are formed. When heated, these lose their water without deflagration, and become insoluble in dilute acids.

The formation of these highly coloured compounds constitutes a characteristic and delicate reaction for stannous salts. In not very dilute solutions, silver nitrate in excess produces a red precipitate; if the solution is very dilute, *e.g.*, 0.001 gram  $\text{SnCl}_2$  per litre, a red coloration is developed after some time. C. H. B.

**Action of Charcoal on a Solution of Gold Chloride.** By G. A. KÖNIG (*Chem. News*, 45, 215).—When purified charcoal is boiled with gold chloride, the gold is deposited in the metallic state on the charcoal, and carbonic anhydride is formed. Lamp-black has a similar action, but apparently less energetic. This action is probably both chemical and physical, the latter depending on the surface and capillary attraction of the charcoal, as lamp-black does not act physically. The chemical action depends on a combustion of carbon into carbonic anhydride. E. W. P.

**Oxidation of Titanic Acid.** By A. PICCINI (*Gazzetta*, 1882, 151—154).—The yellow coloration of titanic acid solutions by hydrogen dioxide was observed by Schönn in 1873, and by Heppe in 1875. To study this reaction more completely, the author added barium dioxide to a cooled solution of titanic acid in sulphuric acid till a drop of the liquid tested with Barreswill's reagent, showed the presence of hydrogen dioxide. The filtered liquid treated with excess of ammonia gave a bulky flocculent precipitate, forming a light yellow powder when washed and dried, and this when heated in the vacuum of a Sprengel pump yielded water and free oxygen. Dilute hydrochloric acid dissolves it, forming a reddish-yellow liquid, with slight evolution of chlorine. Potassium fluoride added to this liquid throws down white potassium fluotitanate, leaving hydrogen dioxide in solution. The dry powder dissolves slowly in cold dilute sulphuric acid, without apparent evolution of gas, and the solution evaporated over sulphuric acid in a vacuum, leaves a syrup which after a few weeks becomes colourless, gives off gas, and deposits a white flocculent substance. Quantitative experiments showed that this decomposition yields 4 parts oxygen to 100 of  $\text{TiO}_2$ ; and this result was confirmed by treating the yellow powder with excess of ammonio-ferrous sulphate, which decolorises it, and determining the excess of the reagent with permanganate. The author is continuing his experiments. H. W.

## Mineralogical Chemistry.

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**Use of Electromagnets for the Mechanical Separation of Minerals.** By L. PEBAL (*Monatsh. Chem.*, 3, 222—223).—This is a criticism of Doelter's recent paper on the same subject (p. 656 of this volume), in which the author points out that the use of an electro-magnet for separating the constituents of rocks was suggested by himself ten years ago (*Mittheil. des naturw. Vereines für Steiermark*, 1872, S. 73). He also objects to Doelter's method of rubbing the pole of the electromagnet in the dry mineral powder, inasmuch as considerable quantities of diamagnetic particles then adhere to those which are attracted by the magnet, and cannot easily be separated. His own method is to move the electromagnet about in water in which the finely pulverised mineral mixture is suspended, and afterwards transfer it with the adhering particles to another vessel of water, the current being then interrupted. After the adhering magnetic particles have separated themselves from the magnet and fallen to the bottom of the vessel, the same course of operations is repeated, in order to ensure as far as possible the separation of the magnetic from non-magnetic particles.

With regard to Doelter's determinations of the relative force with which different minerals are attracted by the magnet, Pebal points out that, besides the more recent investigations of E. Becquerel and G. Wiedermann, Plücker, in 1848, published measurements of the relative intensities of the magnetism and diamagnetism of numerous liquid and solid bodies, including several minerals, made by a method at once simple and well adapted to the purpose (*Pogg. Ann.*, 74, 311; *Jahresb. f. Chemie*, 1874, 48, 249—261). H. W.

**Crystallised Paraffin in Geodes in a Basaltic Lava.** By O. SILVESTRI (*Gazzetta*, 12, 9—11).—In a part of the basaltic lava at Paternò, in the neighbourhood of Etna, small geodes occur about 1 cm. in diameter, filled with solid crystallised paraffin. It is in the form of large yellowish-white pellucid plates of waxy appearance, melting at 56°, and volatile about 300°. It is insoluble in water, almost insoluble in cold, but soluble in boiling alcohol, and very soluble in ether. It was from this same lava that the author formerly extracted a paraffin oil, from which a solid paraffin was separated (this *Journal*, 1877, 1, 704). C. E. G.

**Chemical Nature of Liquid Inclosures found in Crystals of Native Sulphur.** By O. SILVESTRI (*Gazzetta*, 12, 7—9).—Some crystals of sulphur from the Solfara, called "Pozzo in Val Guarnera," in the Province of Catania, Sicily, were found to contain inclosures of a colourless transparent liquid. These crystals are flat laminæ, and between the several laminæ of the crystalline mass a liquid can be seen, as also gaseous bubbles; and if a fragment of one of these laminæ be observed under the microscope, it will be seen to

be traversed by numerous tubular cavities likewise filled with liquid. This liquid was carefully examined and found to be an aqueous solution containing 0.1033 per cent. of saline matter. The percentage composition of the saline mass left on evaporation was found to be 53.527 of sodium chloride, with a trace of potassium chloride, 45.131 of sodium sulphate, and 1.342 of calcium chloride, with traces of barium and strontium chlorides.

C. E. G.

**Polychroic Nuclei of Black Mica.** By A. M. LEVY (*Compt. rend.*, 94, 1196—1198).—The black mica examined occurs abundantly at Latavelet (Saône et Loire) in a rock which traverses the great mass of granite forming the mountains of Mont-Jeu. The plates of mica are sometimes 4 mm. in diameter, and are mixed with a considerable quantity of apatite in greenish or rose-coloured grains. They also contain minute crystals of zircon, about 0.03 mm. in diameter. Round these crystals of zircon are developed polychroic aureoles, which vary from pale yellow to opaque black. The breadth of these aureoles is often double that of the zircon crystal, and their optical properties and direction of maximum absorption are the same as those of the surrounding mica. The aureoles are unaltered at 300°, and they remain visible so long as the mica remains transparent. The nuclei resist the action of hydrochloric acid as long as the surrounding plates of mica, from which it would appear that they owe their origin to a concentration or modification of the ferruginous pigment of the black mica, and are not due to the presence of any organic colouring matter. The aureoles are also developed, although with very feeble intensity, round the grains of apatite.

C. H. B.

**Chemical Researches on the Calcareous Rocks of the Province of Salerno.** By L. RICCIARDI (*Gazzetta*, 1882, 133—147).—The mountains of this province are formed of Apennine limestone, mostly stratified horizontally, but occasionally with slight inclination, as in the group between Angri and Amalfi. This rock is a magnesian limestone, mostly compact crystalline, sometimes amorphous. Fracture scaly, or not unfrequently conchoidal. Colour very variable, from white to blackish-grey. The rock is often veined, and in many parts rich in geodes lined with crystals of calcite. It is fetid in some parts, and almost invariably contains bituminous matter. It takes a high polish, and is much used for building; also for lime-burning. Almost all the varieties dissolve in cold dilute nitric acid, and all with aid of heat, leaving only small residues of carbonaceous matter. The solutions exhibit traces of chlorine, sulphuric acid and iron.

1. AMALFI. *Capo d'Orso*. Ashy-white, very compact; crystalline. Fracture conchoidal.—2. AMALFI. Near the town, the rock is of a dirty white colour and veined; slightly bituminous; fracture conchoidal. Becomes perfectly white on calcination.—3. AMALFI. *Torre*. Ashy-white; cryptocrystalline, spotted with yellow; fracture conchoidal. Contains geodes lined with calcite crystals.—4. Greyish, spotted with yellow; slightly bituminous, with white veins; rich in geodes lined with calcite. Cryptocrystalline, with conchoidal fracture.—5. ATRANI. *Torre Caruso*. Light grey, cryptocrystalline, schistose, with scaly

fracture, slightly bituminous.—6. ATRANI. *Minori*. On the Monicone Pass the rock is dark grey, compact, with conchoidal fracture; bituminous; ashy-white on calcination.—7. ROVELLO. *Torre del Carosello*. Schisto-calcareous, slightly bituminous, blackish-grey. Fracture scaly. Cold nitric acid dissolves it partially, leaving a residue consisting for the most part of carbonaceous matter, with a small quantity of argillaceous substance.—8. MAIORI. *Abazia*. Compact, cryptocrystalline, with conchoidal fracture; colour ash-grey. 9. MAIORI. *Bellagaja*. A mixture of dark grey limestone with shining crystals of calcite.—10. MAIORI. *Salicerchia*. Dark grey, cryptocrystalline, compact, with conchoidal fracture.—11. MAIORI. In the *Nuciata* district the limestone is compact, amorphous, with crystalline fracture, and dark-grey colour.—12. GUARDIOLA (towards Maiori). At *Vera Rossa* the compact limestone is light grey, veined, rich in geodes lined with calcite crystals having red spots. Fracture scaly. Structure cryptocrystalline.—13. CAMAVERDE (towards Maiori). Dark grey; rich in geodes and veins of calcite; cryptocrystalline, with conchoidal fracture; slightly bituminous. Dissolves in hot nitric acid, leaving a small quantity of bituminous substance.—14. ERCHIA. *Ponte*. Cryptocrystalline, compact, with scaly fracture, containing in some parts geodes lined with minute crystals of calcite.—15. CETARA. In some parts dark grey, with yellowish spots; cryptocrystalline, veined with geodes mostly large, lined with calcite crystals; in other parts, ashy-white and crystalline. Both varieties have a scaly fracture, and dissolve in hot dilute nitric acid, leaving in suspension insoluble portions mixed with carbonaceous matter.—16. FUONTE. Ashy-white mixture of amorphous and cryptocrystalline limestone. Compact, with conchoidal fracture; contains geodes lined with minute calcite crystals.—17. RAITI VIETRI. *Fontana a Lemite*. Dark or light grey, amorphous, schistose, or compact crystalline, bituminous, with scaly fracture. The dark grey variety dissolves in cold dilute nitric acid, leaving a gummy residue; the light grey variety dissolves slowly in the cold, completely when heated; both solutions exhibit traces of iron chlorides and sulphates.—18. VIETRI-SUL MARE. Along the coast of this district, on the left, there is a large deposit of travertine, while on the right, the rock is calcareous and schistose, of dark grey colour, bituminous, with scaly fracture.—19. CAVA DEI TERRENI. *Monte Pertuso*. This mountain, like the rest, is composed of horizontal layers of calcareous rock varying in colour from white to dark grey. Three varieties are distinguished: *a*, light; *b*, striped; *c*, dark.—23. MONTE SANT' ANGELO. Composed for the most part of dark grey limestone, (*a*) nearly amorphous, with conchoidal fracture. On the same mountain, however, there occurs another rock (*b*) of ash-white colour, cryptocrystalline, with conchoidal fracture.—21. MONTE CAPRILE. Ashy-white, cryptocrystalline with conchoidal fracture.—22. MONTE CERRETO. This is the highest of the chain, 1313 meters above sea-level. The predominant limestone has a dark grey colour and scaly fracture, and is slightly bituminous.

The paper concludes with a survey of various theories which have been proposed respecting the formation of dolomites, the author inclining to the opinion that they have been deposited at the bottom of

*Analyses.*

	CaO.	MgO.	CO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Insoluble.	H <sub>2</sub> O (at 120°).		Sp. gr.
1 .....	31·04	21·28	47·29	trace	—	—	0·19	=	2·803 at 15°
2 .....	53·86	1·54	14·27	—	—	0·62	0·15	=	2·481 " "
3 .....	33·03	19·48	47·33	—	—	—	0·21	=	2·775 " 16°
4 .....	54·36	1·64	44·02	—	—	—	0·12	=	2·619 " "
5 .....	34·03	18·73	46·47	—	—	—	0·24	=	2·802 " 19°
6 .....	30·82	17·88	43·49	0·73	—	6·69	0·59	=	2·776 " 18°
7 .....	31·01	16·83	43·23	1·14	—	7·95	0·35	=	2·672 " 16°
8 .....	31·21	21·01	47·81	—	—	—	0·08	=	2·821 " 17°
9 .....	30·02	22·03	48·01	—	—	—	0·15	=	2·823 " 16°
10 .....	31·13	21·56	47·61	—	—	—	0·07	=	2·828 " "
11 .....	55·07	0·87	43·41	trace	—	0·97	—	=	2·716 " 19°
12 .....	31·16	21·07	47·57	0·34	—	—	0·14	=	2·827 " 18°
13 .....	31·60	20·78	47·73	—	—	—	—	=	2·815 " 17°
14 .....	31·32	20·80	47·64	—	—	—	0·21	=	2·831 " 19°
15 dark .....	30·13	22·11	47·29	0·12	—	0·63	—	=	2·836 " 16°
16 — light .....	33·04	18·64	46·05	trace	—	1·94	—	=	2·803 " "
17 dark .....	34·64	17·47	47·14	—	—	—	0·17	=	2·717 " "
18 — light .....	30·55	21·98	47·35	—	—	trace*	0·09	=	2·782 " "
19 a .....	31·37	19·13	46·03	—	—	3·68*	—	=	2·805 " "
19 b .....	34·84	18·09	47·15	—	—	—	—	=	2·801 " 17°
19 c .....	32·64	20·38	47·02	—	—	—	—	=	2·807 " "
20 dark .....	33·84	18·64	47·16	—	—	0·47	—	=	2·804 " "
20 — light .....	54·13	2·01	44·17	—	—	0·58	—	=	2·693 " 16°
21 .....	36·64	16·30	46·63	—	—	—	—	=	2·792 " 17°
22 .....	32·63	19·82	47·72	—	—	—	0·24	=	2·778 " 20°
22 .....	34·24	18·47	46·39	—	—	—	0·18	=	2·803 " 16°

\* Carbonaceous matter.

the sea, and subsequently elevated. Their density increases with the proportion of magnesium carbonate. H. W.

**Chemical Composition of Vesuvian Pumices collected on Monte Sant' Angelo.** By L. RICCIARDI (*Gazzetta*, 1882, 130—132).—The Apennine limestones of the chain of mountains of which Monte Sant' Angelo forms a part, are strewn with vesuvian pumice, both on the side facing the volcano and on the opposite side. The parts on which they occur are clothed with a luxuriant vegetation, while the other parts are barren.

The pumices exhibit the usual porous character, and float on water. The ground-mass is amorphous, of greenish-yellow colour, and rich in fragments of leucite and augite, sometimes in well-defined crystals several millimeters long, with traces of mica and pyrites.

The composition of these minerals is as follows:—

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.
Augite	50·43	4·03	21·34	12·87	11·21	—	— = 99·88
Leucite	55·37	24·02	—	—	—	20·52	trace = 99·91

Sp. gr. at 20°: of the augite, 3·42; of the leucite, 2·48.

The pumice, even when reduced to very fine powder, is not attracted by the magnet, but when calcined it solidifies to a brick-red compact mass, slightly attracted by the magnet, losing at the same time about 3·35 per cent. of its weight, which may be regarded as water of hydration. The moistened powder turns red litmus-paper blue. The pumice is completely decomposed by sulphuric and nitric acid, partially by hydrochloric acid, with evolution of hydrogen sulphide, a fact which corroborates the presence of pyrites. The composition of the pumice, as determined by the mean of three analyses, is the following:—

SiO <sub>2</sub> .....	52·26	CaO .....	6·64
P <sub>2</sub> O <sub>5</sub> .....	0·94	MgO .....	1·86
SO <sub>3</sub> .....	0·22	Na <sub>2</sub> O .....	1·63
Cl .....	0·42	K <sub>2</sub> O .....	8·83
Al <sub>2</sub> O <sub>3</sub> .....	16·99	Loss by ignition .....	3·33
Fe <sub>2</sub> O <sub>3</sub> .....	2·13		
FeO .....	5·22		
			<hr/> 100·47

Sp. gr. = 1·218 at 20°.

The occurrence of this volcanic material in a district whose mountains are wholly composed of magnesium limestone rock, explains the fact that tobacco and acid fruits flourish in all the alluvial soils between Scafati and Cava dei Terreni. Acid fruits form indeed one of the chief articles of exportation from the coast of Amalfi.

H. W.

**Two Japanese Meteorites.** By E. DIVERS (*Chem. News*, 45, 206).—These meteorites, which fell in Japan about 150 years ago, are irregular quadratic pyramids, and evidently fragments. Faintly marked thin ridges and streaks are to be seen on both sides; the

edges and faces are rounded off, and are covered with the usual thin black coating. The interior is light grey in colour, earthy, porous, soft, and interspersed with particles of metallic iron and its sulphide. The black coating yields sulphuretted hydrogen when treated with hydrochloric acid. The weight of the larger fragment is 5·6 kilos., that of the lesser 4·6 kilos., and they have a sp. gr. 3·62.

*Composition.*

Fe.	Ni, &c.	Mn.	Sn, &c.	FeS.	FeCr <sub>2</sub> O <sub>4</sub> .	P <sub>2</sub> O <sub>5</sub> .	SiO <sub>2</sub> .	MgO.
15·35	1·75	0·18	0·15	5·91	0·61	0·34	36·75	23·36
FeO								
(as silicate).	CaO.	Al <sub>2</sub> O <sub>3</sub> .	Na <sub>2</sub> O.	K <sub>2</sub> O.	MnO.	NiO.		
8·64	1·94	1·89	0·97	0·16	0·51	0·30	= 99·01	

*Mineralogically Arranged.*—Nickel iron, 17·43; iron sulphide, 5·91; silica, soluble in HCl, olivin, 32·89 (SiO<sub>2</sub> = 13·10); silicates insoluble in acid, 43·16 (SiO<sub>2</sub> = 24·30); iron chromite, 0·61.

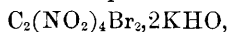
These meteorites therefore belong to that class which contains three-tenths of their weight of iron in the free and combined states. Comparing the analyses with those of meteorites in other parts of the world, their compositions are found to be very similar.

E. W. P.

## Organic Chemistry.

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**Tetranitro-ethylene Bromide.** By A. VILLIERS (*Compt. rend.*, **94**, 1122—1124).—Ethylene bromide is mixed in a retort with about an equal volume of fuming nitric acid, and the mixture heated, when an energetic reaction takes place, with evolution of oxides of nitrogen, nitrosyl bromide and bromine. At first, the ethylene bromide dissolves in the acid, but after a time the liquid becomes turbid, and separates into two layers. At this point the reaction tends to become explosive, the lamp must be withdrawn, and the retort cooled by means of cold water. The liquid is afterwards distilled almost to dryness. Often when the lamp is withdrawn and the temperature of the mixture consequently lowered, the reaction again becomes explosive. The distillate is mixed with the liquid left in the retort, and washed first with water, then with dilute sulphurous acid, and finally with water. A large quantity of potash is now dissolved in the liquid with agitation, when a yellow mass is formed. After standing 24 hours, the still liquid portion is decanted off, the crystals dried, and recrystallised from warm water. The compound thus obtained,



forms brilliant canary-yellow crystals, only slightly soluble in cold, but somewhat soluble in hot water; insoluble in absolute alcohol, ether, &c.; sp. gr. at  $14^\circ = 1.25$ . When exposed to light, it undergoes a molecular



change, being converted into a yellowish-brown substance. When heated to  $145^{\circ}$  (a temperature below the detonating point of mercury fulminate,  $186^{\circ}$ ), it detonates, with evolution of oxides of nitrogen and formation of potassium bromide. It does not explode by percussion. With solid potassium hydroxide, it yields an unstable red compound. Dilute acids liberate tetra-nitro-ethylene bromide, an unstable liquid.

C. H. B.

**Mercury Fulminate.** By E. CARSTANJEN and A. EHRENBURG (*J. pr. Chem.* [2], **25**, 232—248).—When fulminate of mercury is treated with concentrated hydrochloric, hydrobromic, or hydriodic acid, it yields, besides a mercury salt and carbonic anhydride, a *hydroxylamine* salt, and when hydriodic acid is used, ammonium iodide. With hydrochloric acid, 50 grams fulminate gave 16.5 grams pure hydroxylamine hydrochloride. Dilute sulphuric acid, 1:5, does not act on fulminate of mercury in the cold, but on boiling there is a copious evolution of gas, principally carbonic anhydride, and precipitation of mercury *oxalate*, the solution containing ammonium and hydroxylamine sulphate. The action of oxalic, tartaric, and acetic acids on mercury fulminate are being investigated, but the investigation is not yet complete; a hydroxylamine salt, however, seems always to be produced. When mercury fulminate is mixed with thiocyanic acid, there is development of much heat, carbonic anhydride is evolved, and a blackish precipitate of mercury sulphide, mixed with metallic mercury, is formed, whilst a mercury compound not yet examined remains in solution. Thiocarbamide also acts energetically on the fulminate, the temperature rising to the boiling point of the liquid, whilst carbonic anhydride is given off. If this experiment is conducted carefully, an oil forms, which solidifies and crystallises from warm water in snow-white crystals. Hydrocyanic acid dissolves the fulminate without evolution of gas, and mercury and ammonium cyanides are formed amongst other products: this experiment is incomplete.

To solve the question which form of cyanogen is present in mercury fulminate, several reduction experiments were tried. With zinc and dilute sulphuric or hydrochloric acid, or zinc dust and ammonia, all the carbon-atoms are removed, and carbonic anhydride and ammonia salts are produced. By treatment with sodium-amalgam, the mercury seems to be replaced by sodium, the product, however, containing a mixture of two sodium salts, a white and a yellow; the latter is more soluble in aqueous alcohol than the white, affording a means of separating them. They have similar properties: they are both explosive, give numbers approximating to those for sodium fulminate, show V. Meyer's reaction for nitrolic acids, and evolve hydrocyanic acid when treated with hydrochloric acid. The yellow and white *lead salts* are precipitated from the corresponding sodium salts: the yellow lead salt is converted into the white by treatment with the original product. The white lead salt explodes on heating or by percussion; the yellow salt deflagrates like gunpowder when heated, but does not explode by percussion. With the original product, mercury chloride gives at first a heavy white precipitate, and afterwards an orange-yellow one. The white salt is apparently mercury fulminate, mixed with a little sodium salt; the yellow salt has not as yet been examined. Silver nitrate at first pre-

precipitates a white gelatinous body which explodes very violently when dry; further addition of the nitrate brings down a brown-red precipitate. Copper sulphate gives a green, and then a yellow-brown precipitate; thallium a brown and then a yellow; and barium, calcium, and magnesium salts, white precipitates. A mixed solution of ferrous and ferric salts produces a small quantity of a brown precipitate, which redissolves on shaking, but a further addition of iron salts renders the precipitate permanent, and a large quantity of iron salt goes into solution, which becomes yellow; the iron cannot be precipitated by ammonium sulphide: by continuing the addition of iron salts, a point is suddenly reached, when the liquid becomes very hot, and of a violet-red colour, ammonia and carbonic anhydride are given off, and a dark brown powder separates. If the reaction is violent, the greater part of the iron is precipitated, the solution assumes a pale rose-red colour, and shows the nitroprusside reaction with ammonium sulphide. If, however, the addition of iron salts is stopped before the violet colour appears, and the liquid is filtered, no iron can be detected in the filtrate by ammonium sulphide, and it gives a deep violet-red coloration with very dilute ferric chloride solution. The yellow solution also gives a violet-red coloration with acids, but is not as sensitive as with ferric chloride. A violet-red solution is also obtained when mercury fulminate is boiled with potassium ferrocyanide. Experiments made to replace the mercury in the fulminate by hydrocarbon residues, by means of ethyl iodide, gave rise to explosions, mercury iodide being formed. When the product of the action of sodium-amalgam on mercury fulminate is treated with potassium-ethyl sulphate and evaporated, it gives off a strong nitril odour.

D. A. L.

**Additions to the Researches on Etherification.** By N. MENSCHUTKIN (*Jour. Russ. Chem. Soc.*, April, 1882, 162—169).—In the present paper, which is to be regarded as the last of the author's investigations on this subject, continued from 1876—1881, he first gives a summary of his work; then follow some experiments, made after the publication of the various chapters. Instead of alcohols or acids, the author investigated their substitution-products.

*Primary alcohols: Glycol-monochlorhydrin.*—On heating it with acetic acid, an irregular reaction takes place, owing to partial decomposition. The same is the case with *glyceryl dibromhydrin* and *propargyl alcohol*.

*Secondary alcohols (with acetic acid). Ethyl-isobutyl carbinol.*—Initial velocity = 18·23; limit = 63·06, in accordance with the secondary character of the compound. *Menthol*: Initial velocity = 15·29; limit = 61·49. The author's view that the "variable constituents" of this secondary alcohol contain, the one 3, and the other 6 atoms of carbon, is in accordance with Atkinson's results (this Journal, Trans., 1882, 49). Atkinson's opinion, that the radical  $\left. \begin{matrix} \text{C}_6\text{H}_{11} \\ \text{C}_3\text{H}_7 \end{matrix} \right\} \text{CH.OH}$ , is derived from hexhydrobenzene, as shown by his optical researches, agrees with that of Kanownikoff. The secondary alcohol, *borneol*, shows an initial velocity of 25·12, whereas that of *ethyl-phenyl carbinol* is = 18·89, both

undergoing decomposition on further heating. *Diphenylcarbinol*: Initial velocity = 21.99.

*Tertiary Alcohols*.—A remarkably slow etherification is shown by *ethyl-dimethyl carbinol* with acetic acid at 100°; the action does not begin until after a week's heating, and in 45 days a limit of 5.75 is reached.

As *substituted acids*, *monochloracetic* and *dichloracetic acid* (with isobutyl alcohol) were investigated, but without much success, decomposition taking place. Only an initial velocity of 64.42 was found for the first acid, showing that the rate of etherification increases rapidly when the hydrogen in acetic acid is replaced by chlorine. With *nitrobenzoic acid* and isobutyl alcohol, the rate of etherification increases on replacing the hydrogen by a nitro-group, the value being = 24.76 for nitrobenzoic, and only = 8.62 for benzoic acid, whereas the limits of both acids are the same, 72.28 and 72.57 respectively. The author is now engaged in investigating the phenomena of dissociation of ethereal salts of tertiary alcohols. B. B.

**Oxidation of Glycerol by Potassium Permanganate.** By G. CAMPANI and D. BIZZARRI (*Gazzetta*, 12, 1—7).—The authors have subjected glycerol to oxidation by cupric hydroxide under the same conditions as those by which Claus (*Annalen*, 147, 114) succeeded in obtaining tartronic acid from glucose, but the product was an uncrystallisable gummy matter. Attempts to oxidise glycerol with lead permanganate and acetic acid were equally unsuccessful, but better results were obtained with potassium permanganate in alkaline solution, tartronic acid being invariably produced, although in small quantity. To a solution of 50 grams glycerol and 300 of potash in 6000 of water, 67 grams of potassium permanganate were gradually added in the course of three days; the whole was allowed to remain four days longer, then filtered from the precipitated manganese oxide, acidulated with acetic acid, and precipitated with lead acetate. The lead precipitate, when decomposed by hydrogen sulphide in the usual way, gave a filtrate, from which oxalic and tartronic acids were separated by fractional crystallisation. Acetic, formic, and propionic acids are also formed in this reaction.

In another experiment, in which a larger quantity of water (10 litres) was employed, and the mixture kept cool by ice, crystals were obtained, which had the composition of manganese tartronate,  $[\text{COOH}.\text{CH}(\text{OH}).\text{COO}]_2\text{Mn}$ . They belong to the triclinic system,  $a : b : c = 58.5 : 47 : 42$ . Observed faces 010, 100,  $\bar{3}40$ , 011,  $30\bar{2}$ , the face 010 being usually the most developed. For the sake of comparison, manganese tartronate was prepared with the acid obtained by the decomposition of nitrotartaric acid, and was found to be identical with the above, both chemically and crystallographically. The tartronic acid begins to melt at 179—180°, and fuses completely at 185°, with the abundant evolution of gas described by Dessaignes, and characteristic of the decomposition of tartronic acid. C. E. G.

**Maltose.** By E. MEISSL (*J. pr. Chem.* [2], 25, 114—130).—The specific rotatory power of maltose has been determined by many

observers, whose results, however, do not agree very closely; this disagreement is no doubt due to the difficulties of reading when ordinary light is used; but with the sodium flame as source of light these difficulties are avoided: indeed one observer made his experiments with a sodium flame, but unfortunately in calculating his results he employed an incorrect formula, and did not give sufficient data for their subsequent rectification. On making experiments with various preparations of maltose, and using a sodium flame, the author finds that its specific rotatory power varies inversely with the temperature and concentration; as a mean of several experiments he gives the following equation for the specific rotatory power of maltose with the sodium flame;  $[\alpha]_D = 140.375 - 0.01837 P - 0.095 T$ , where  $T$  represents the temperature and  $P$  the percentage of maltose in the aqueous solution. As previously shown by the author, maltose possesses birotatory powers, 15—20° difference being observable between freshly prepared and stale or heated solutions; and for solutions lying between 5—40 per cent., the percentage of maltose may be accurately found by multiplying by the factor 0.362, the degree of rotation obtained at 17.5°, a tube 200 mm. long being employed. The assimilation of the elements of water to maltose is attended with much greater difficulty than in the case of cane-sugar, and its conversion into dextrose is best attained by three hours' heating with a 3 per cent. solution of sulphuric acid; under the most favourable conditions, however, only 98.5 per cent. of the maltose can be converted into dextrose, as a point is arrived at where the destruction of the ready formed dextrose proceeds with greater rapidity than the formation of fresh dextrose.

Chlorine does not act so strongly on maltose as on dextrose or saccharose; an acid, however, is formed, which differs from gluconic and glycollic acids.

J. K. C.

### On Arabinose, Erythrol, Mannitol, Lævulan, and Lævulose.

By P. CLAESSON and others (*Bied. Centr.*, 205—207).—Kiliani (Abstr., 1881, 243) considered that arabinose and lactose are identical, but Claesson, although not denying the identity of the sugar from gum arabic with lactose, does not admit that arabinose is the same as lactose, and he states that there are kinds of gum which, when boiled with acid, yield a sugar resembling lactose, whilst other gums yield arabinose, and when oxidised by nitric acid, form no mucic acid, and are dextrorotatory.

Przybytek having oxidised erythrol, has obtained oxalic acid, and another acid resembling tartaric acid; this forms soluble salts with potash and ammonia, and when heated to 170—175° is converted into racemic acid. According to Hecht and Iwig, when mannitol is oxidised by potassium permanganate, it yields formic, oxalic, and tartaric acids, and a sugar which reduces Fehling's solution, and not a tribasic acid (dioxysocitric acid), as stated by Pabst. Under the name lævulan, Lippmann describes a carbohydrate analogous to dextran, and which is lævorotatory to nearly the same extent as dextran ( $[\alpha]_D = -221^\circ$ ). Lævulan does not reduce Fehling's solution, and when oxidised yields mucic acid; heated with sulphuric acid at 120°, it yields lævulose, which when mixed with dextrose produces a substance undistinguish-

able from inverted sugar. The gelatinisation of lævulan in water recalls Payen's gelose and Reichardt's pararabin. Viscose described by Béchamp seems to be identical with Scheibler's dextran. Scheibler distinguishes lævulose from dextrose by the fact that the former, under the influence of nascent hydrogen, is converted into mannitol. According to Jungfleisch and Lefranc, when inulin is converted into lævulose by sulphuric acid, and the solution purified by alcohol and ether, acicular crystals of lævulose can be obtained. E. W. P.

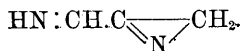
**Saccharin.** By H. KILIANI (*Ber.*, 15, 701).—Amongst the products of the action of calcium hydroxide on invert sugar, the author obtained a substance identical with saccharin in melting point, rotatory power, and composition. By the oxidation of saccharin with silver oxide, acetic and glycollic acids are formed; it thus differs from dextrose and lævulose, which give oxalic, formic, and glycollic acids. From this result, it would appear that saccharin contains a methyl group, a view which is further confirmed by the fact that by the oxidation of saccharin by permanganate, not only carbonic acid and water, but also acetic acid is formed. V. H. V.

**Attempts to prepare Secondary and Tertiary Amines of Secondary Alcohol-radicles.** By H. JAHN (*Monatsh. Chem.*, 3, 165–172).—It is well known that the action of ammonia on primary moniodo-paraffins gives rise to the four possible compounds up to the tetra-alkylammonium iodide. But with the secondary moniodo-paraffins the case is different, all attempts hitherto made to obtain in this manner a secondary or tertiary amine\* of a secondary alcohol-radicle having yielded nothing but the primary amine, together with the corresponding olefine and its polymerides. In like manner, S. Reymann found that when the monobutylamine,  $\text{CHMe}_2\text{CH}_2\text{NH}_2$ , produced by the action of sulphuric acid on secondary butyl thiocarbimide, was heated with secondary butyl iodide, scarcely a trace of a di- or tri-butylamine was obtained, the product consisting almost wholly of butylene and polybutylenes (this Journal, 1875, 141); and Uppenkampf (*Ber.*, 8, 57) by treating secondary hexyl iodide (from mannite) with alcoholic ammonia, obtained nothing but the primary amine, together with hexylene and polyhexylenes.

These results are fully corroborated by the experiments described in the present paper on the action of ammonia on the iodides of secondary propyl, hexyl, and octyl. Moreover the monoctylamine obtained by the author from the secondary octyl alcohol was not altered by heating it in sealed tubes, either with octyl iodide or with amyl iodide, and was but very slowly attacked by methyl iodide; by repeated digestion, however, the base being at each time set free, and then treated with fresh methyl iodide, it was ultimately converted into the iodide of octyltrimethylammonium. H. W.

\* In the original paper these bases are spoken of as *diamines* and *triamines*; but this is incorrect; a diamine contains 2 at. and a triamine 3 at. nitrogen, being derived respectively from the types  $\text{N}_2\text{H}_6$  and  $\text{N}_3\text{H}_9$ .—H. W.

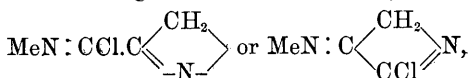
**Glyoxaline.** By N. LJUBAVIN (*Jour. Russ. Chem. Soc.*, April, 1882, 161).—Referring to H. Goldschmidt's paper on glyoxaline (*Berl. Ber.*, **14**, 1844), the author gives several reasons which lead him to the assumption of the following constitutional formula for this compound:—



B. B.

**Oxaline and Glyoxaline.** By O. WALLACH (*Ber.*, **15**, 644--652).—In a former communication (*Abstr.*, 1881, 572) the author has described an oxalmethylene (b. p. 197°) obtained from chloroxalmethylene, while Goldschmidt, by the distillation of dimethylglyoxaline hydroxide, has prepared a methylglyoxaline, apparently identical with the author's oxalmethylene. In order to examine further the identity of these substances, the author has prepared methylglyoxaline by the direct combination of glyoxaline with methyl iodide, and finds that the substance so obtained is identical in its chemical and physical properties with oxalmethylene.

From the author's researches on the formation of oxaline, it would appear probable that chloroxalmethylene is derived from an imid-chloride,  $\text{MeN}:\text{CCl}.\text{CCl}:\text{NMe}$ , by the removal of a molecule of hydrochloric acid, which gives for chloroxalmethylene the formula—



of which the former, containing an amidochloro-group,  $\text{CCl}:\text{NMe}$ , would presuppose a weakness of affinity of the chlorine-atom, whereas the chlorinated oxalines are very stable substances. Adopting then the second formula for chloroxalmethylene or methylglyoxaline, the constitution of glyoxaline will be  $\text{NH}:\text{C} \begin{array}{c} \nearrow \text{CH}_2 \\ \searrow \end{array} \text{N} \begin{array}{c} \nearrow \text{CH}_2 \\ \searrow \end{array} \text{CH}$ .

Although the identity of methylglyoxaline and oxalmethylene is established, yet, if these constitutional formulæ be correct, it does not therefore follow that the higher homologues, prepared by different processes, as for instance oxalethyline,  $\text{C}_6\text{H}_{10}\text{N}_2$ , and propylglyoxaline,  $\text{C}_8\text{H}_{14}\text{N}_2$ , should be identical.

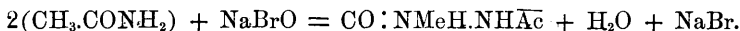
To examine this question, the author prepared propyl and amylglyoxaline by the action of propyl and amyl bromide on glyoxaline, and finds that they are not identical with oxalethyline and oxalpropylene.

Oxaline.		Glyoxaline.	
	Boiling point.		Boiling point.
$\text{C}_4\text{H}_6\text{N}_2$ ..	197°	$\text{C}_4\text{H}_6\text{N}_2$ ..	197°
$\text{C}_6\text{H}_{10}\text{N}_2$ ..	212—213°	$\text{C}_6\text{H}_{10}\text{N}_2$ ..	219—223°
$\text{C}_8\text{H}_{14}\text{N}_2$ ..	229—230°	$\text{C}_8\text{H}_{14}\text{N}_2$ ..	240—245°
	Soluble in water.		Insoluble in water.
	Sp. gr.		Sp. gr.
	1·0360		1·0360
	0·9820		0·9670
	0·9520		0·9400

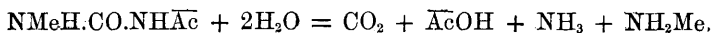
The properties of bases of the oxaline and glyoxaline series are compared in the table.

V. H. V.

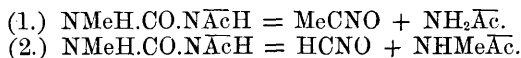
**Action of Bromine in Alkaline Solutions on Amides.** By A. W. HOFMANN (*Ber.*, 14, 2725—2736).—By the action of sodium hydroxide on a solution of acetamide in bromine, *acetylmethylcarbamide* is obtained as follows:—



This compound forms colourless prismatic crystals (m. p. 180°), sparingly soluble in cold, more easily in hot water, and slightly soluble in alcohol and ether. Heated with water at 150°, it is decomposed as follows:—

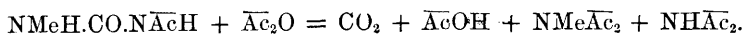


Acetylmethylcarbamide, when heated above its melting point, undergoes a series of decompositions, and amongst the products the following have been found: carbonic anhydride, ammonia, methylamine, acetamide, methylacetamide, dimethylic and trimethylic cyanurate. From these two last-mentioned bodies, which form a sublimate in the neck of the retort in which the operation is conducted, the author has separated dimethyl cyanurate by means of its silver salt. It crystallises from hot water in colourless needles, m. p. 222°; by heat, it is converted into methyl cyanate, and alkalis convert it into methylamine and ammonia. The formation of these bodies may be explained by supposing acetylmethylcarbamide to be decomposed by heat as follows:—



The trimethyl cyanurate owes its formation to the polymerisation of methyl cyanate, and dimethyl cyanurate to the association of cyanic acid and methyl cyanate. The presence of acetamide and methylacetamide in the distillate obtained by heating acetylmethylcarbamide, was shown by fractionating the said distillate. Acetamide boils at 220°, and melts at 82—83°. (The author regards the m. p. 78—79°, which is usually given, as too low.) Methylacetamide boils at 207° and melts at 26°; when prepared from ethyl acetate and methylamine, it was found to boil at 206° and melt at 28°.

By heating acetylmethylcarbamide with acetic anhydride to boiling, and fractionating the product, diacetamide and methyl diacetamide were obtained, thus:—



Methyl diacetamide is a liquid boiling at 192°; when treated with aniline it yields phenylacetamide and acetamide, thus:—



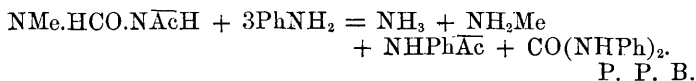
Diacetamide was obtained from the portion boiling above 210°; it is a crystalline body melting at 82°, *i.e.*, at the same temperature as

monacetamide. Besides the method adopted by Strecker (*Annalen*, **103**, 321), the action of caustic soda may be utilised, by which diacetamide is alone acted on; further, acetamide is much less soluble in ether and light petroleum than the diacetamide. The author regards the low melting points given by Gautier (*Compt. rend.*, **47**, 1255) and Wichelhaus (*Ber.*, **3**, 847) for diacetamide, as due to the presence of acetamide. Contrary to the generally accepted view, both acetamide and diacetamide have been found to have a neutral reaction towards vegetable colouring matters.

Concentrated sulphuric acid decomposes acetylmethylcarbamide into acetic acid, ammonium sulphate, and methylamine sulphate, and the methene disulphonic acid described by Buckton and Hofmann (*Annalen*, **100**, 35).

By boiling with concentrated hydrochloric acid, this substituted carbamide is converted into acetic acid and monomethylcarbamide (m. p. 100–101°), and by prolonged boiling, carbonic anhydride, methylamine, and ammonia are formed. Concentrated nitric acid produces a similar decomposition, the carbamide uniting with the excess of acid to form the nitrate of monomethylcarbamide.

Caustic alkalis resolve this acetylmethylcarbamide into carbonic anhydride, acetic acid, ammonia and methylamine. When treated with aniline it forms ammonia and methylamine, acetanilide, and diphenyl carbamide, thus:—



**Conversion of Carbon Oxysulphide into Carbamide and Thiocarbamide.** By BERTHELOT (*Compt. rend.*, **94**, 1069–1070).—The author has previously shown that carbon oxysulphide combines with ammonia, forming ammonium oxythiocarbamate, which is readily transformed into carbamide, with elimination of hydrogen sulphide. When the aqueous solution of the oxythiocarbamate is evaporated by heat, a crystalline product is obtained which consists mainly of carbamide with a notable quantity of thiocarbamide and a little ammonium thiocyanate. The formation of thiocarbamide is either due to the existence of two isomeric oxythiocarbamates,  $\text{CONH(SH).NH}_3$  and  $\text{CSNH(HO).NH}_3$ , or is the result of two simultaneous decompositions of the oxythiocarbamate, in one of which it loses water and in the other hydrogen sulphide.

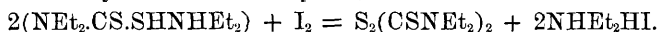
C. H. B.

**Ethylated Thiocarbamides.** By M. GRODZKI (*Ber.*, **14**, 2754–2758).—*Triethylthiocarbamide*,  $\text{NHEt.CS.NEt}_2$ . The formation of this body was observed in the separation of ethylamine and diethylamine by means of Hofmann's method (*Ber.*, 1868), which depends on the fact that when treated with carbon bisulphide, these bases form thiocarbamates, of which, on treatment with metallic oxide, the ethylamine and ethyl thiocarbamate alone form a thiocarbamide. In performing this separation, the author obtained the above thiocarbamide by extracting the lead sulphide with ether. It is insoluble in water, but soluble in alcohol and ether; it forms a thick oily liquid which crystal-



lises on standing (m. p.  $26^{\circ}$ ), and distils at  $205^{\circ}$ , with slight decomposition. When heated with phosphoric anhydride, it forms ethylthiocarbamide, and when fused with potash, yields mono- and di-ethylamine. Its formation is due to the action of diethylamine on ethylthiocarbamide.

*Tetrethylthiocarbamide*,  $\text{CS}(\text{NEt}_2)_2$ , is obtained by heating the triethylcarbamide with ethyl iodide in sealed tubes at  $100^{\circ}$ , and decomposing the crystalline product with soda. It is a colourless liquid (b. p.  $216^{\circ}$ , sp. gr. =  $0.9345$  at  $15^{\circ}$ ), insoluble in water, but soluble in alcohol, ether, and acids. It is a strong base, having an alkaline reaction, and expelling ammonia from its salts. Heated with phosphoric anhydride, it yields no thiocarbamide; it is not attacked by potash solution, but when fused with potash, it yields diethylamine. Nitric acid has but very little action on it. Attempts to prepare tetrethylthiocarbamide from diethylamine and diethyl carbamate, have proved futile; when this compound is treated with iodine it yields a diethylthiuramide bisulphide, thus:—



This compound is insoluble in water, easily soluble in hot alcohol, but insoluble in ether (m. p.  $70^{\circ}$ ). It is insoluble in hydrochloric acid and soda, and but slightly attacked by these, but when fused with potash it yields diethylamine.

P. P. B.

**New Method for obtaining Oxymethylene.** By I. KABLOUKOFF (*Jour. Russ. Chem. Soc.*, 1881, 194—195).—The author prepared large quantities of oxymethylene (methaldehyde) by passing a mixture of air and vapour of methyl alcohol through a glass tube filled with platinised asbestos and heated in a combustion furnace. The author intends to investigate this compound, its isomerides, liquid and solid, and the products of its transformation.

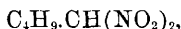
B. B.

**Action of Zinc Ethide on Butylchloral.** By K. GARZAROLLI-THURNLACKH (*Ber.*, 14, 2759—2761).—Butylchloral and zinc ethide yield primary trichlorobutyl alcohol, which crystallises in prisms, m. p.  $61.5^{\circ}$ , and on oxidation yields trichlorobutyric acid. Acetic chloride and trichlorobutyl alcohol yield trichlorobutyl acetate, a liquid heavier than water, boiling at  $130$ — $132^{\circ}$  under a pressure of  $70$  mm.

The remainder of this communication consists of remarks on Wagner's claim (*Ber.*, 14, 2556) to reserve for himself the study of the action of zinc ethide on substituted aldehydes.

P. P. B.

**Dinitro-derivatives from Ketones.** By G. CHANCEL (*J. pr. Chem.*, 25, 271—272).—By the action of concentrated nitric acid on diethyl ketone, the author obtained, besides propionic acid, dinitroethane,  $\text{C}_2\text{H}_4(\text{NO}_2)_2$  (*Compt. rend.*, 87, 1405). In a similar manner, he has now obtained dinitropropane, dinitropentane, dinitrobutane, and dinitrohexane, respectively from dipropyl, diamyl, dibutyl, and methylhexyl ketones. The first two nitro-derivatives are identical with the ordinary bodies of the same name. *Dinitropentane*,



is an oily heavy liquid. Its *potassium-derivative*,  $C_4H_9.CK(NO_2)_2$ , crystallises from water in brilliant yellow leaflets. The *silver-derivative* is similar, but only sparingly soluble. By reduction, dinitropentane is resolved into valeric acid, ammonia, and hydroxylamine. *Dinitrobutane* is the lower homologue of the above, and resembles it. The *potassium-derivative* crystallises in yellow prisms. *Dinitrohexane*,  $C_6H_{11}.CH(NO_2)_2$ , is a heavy oil; its potassium-derivative forms yellow leaflets. When reduced, it yields caproic acid, ammonia and hydroxylamine. It is only ketones having at least one primary radical,  $CH_2R'$ , which yield a fatty acid and a dinitro-derivative.

D. A. L.

**Basic Magnesium Acetate.** By W. KUBEL (*Ber.*, **15**, 684—686).—When an aqueous solution of magnesium acetate is warmed with ignited magnesia, the latter is converted into its hydroxide, and subsequently dissolves to a great extent to form an alkaline liquid, which is a solution of basic magnesium acetate. Solutions of this salt possess to a remarkable degree antiseptic, disinfecting, and deodorising properties, instances of which are mentioned in the paper. A thick solution of basic magnesium acetate, containing magnesium hydroxide in suspension, has been introduced into commerce.

V. H. V.

**Reactions of the Acetates of Chromium, Iron, and Aluminium.** By B. REINTZER (*Monatsh. Chem.*, **3**, 249—265).—Ferric and aluminic salts, boiled with a quantity of sodium acetate sufficient to convert them into acetates, deposit the whole of the iron and aluminium as basic acetates, probably in consequence of the resolution of the normal acetates formed in the first instance, into basic salts and free acetic acid. Respecting the behaviour of chromic salts under similar circumstances, the statements of different authors do not quite agree. Schiff (*Annalen*, **124**, 168) states that when normal chromic acetate is boiled with water, no decomposition takes place; whereas, according to O. Wallach (*Tabellen zur. chem. Analyse*, 1880), chromic salts, like the salts of iron and aluminium, yield, when boiled with sodium acetate, a precipitate of chromic acetate.

According to the author's experiments, a solution of chromic chloride or sulphate, boiled with excess of sodium acetate, yields no precipitate. If the boiling be continued for a short time only, the solution turns violet on cooling; and in the solution thus altered no precipitate is formed by potash, soda, ammonia, ammonium hydro-sulphide or carbonate, sodium phosphate, barium hydroxide, or barium carbonate. Potash, soda, and baryta turn the solution green, and after 12 to 24 hours, convert the liquid into a green jelly; ammonia forms a violet jelly. The precipitation is accelerated by heat in all cases except with sodium phosphate, which forms no precipitate, even when aided by heat.

A similar passivity towards the reagents above mentioned is imparted by the chromic solution to a certain quantity of ferric or aluminic acetate. Neither by heating to the boiling point nor by addition of caustic alkalis or ammonia, or their salts, can ferric or aluminic acetate be detected in presence of chromic acetate. In such a mixed solution, ammonium sulphide alone produces a slow but com-

plete precipitation of the iron, whereas alumina is not completely precipitated in the cold by any reagent whatever. A given quantity of chromium, however, can protect from precipitation only a limited quantity of ferric oxide or alumina; and, what is especially remarkable, it can protect a considerable quantity only when the chromic solution has been boiled with the sodium acetate before the addition of the ferric or aluminic solution. From these results, it follows that, in presence of chromic salts, the method of separation founded on the precipitation of iron and aluminium in the form of basic acetates, becomes utterly useless, either for qualitative or for quantitative analysis.

The influence of a chromic salt on the precipitation of ferric or aluminic salts varies to a certain extent according as to whether it is in the violet or the green modification. When a green solution of chromic acetate is mixed with a small quantity of ferric acetate, and the mixture is boiled, the iron is separated in the form of a flocculent precipitate; but if a solution of ferric acetate be added to an originally violet solution of chromic acetate and the mixture boiled, then, whatever may be the quantity of ferric solution added, no precipitation of iron will take place. Exactly the same is the case with a violet solution of chromic acetate obtained by boiling a green solution with sodium acetate; also with a green chromic acetate solution boiled without any addition. Green chromic acetate, therefore, acts like most metallic salts when heated, in precipitating a solution of ferric acetate; whereas violet chromic acetate, so far from producing a precipitate, even renders a large portion of the iron acetate as indifferent towards reagents as itself. Thus, when a violet solution or a boiled green solution of chromic acetate is boiled with a moderate quantity of ferric acetate solution, sodium acetate may then be added and the liquid boiled, without precipitation of the iron. Neither is any action produced in such solutions for a long time at ordinary temperatures by any of the reagents—such as caustic alkalis, ammonia, caustic baryta, alkaline carbonates and phosphates, barium carbonate, or potassium ferrocyanide—which precipitate ferric salts under normal circumstances, precipitation not taking place indeed until after several hours' boiling. The quickest action is produced by ammonium sulphide; but even in this case a decided retardation takes place, as compared with the rate of precipitation in pure solutions of ferric acetate. If the quantity of ferric acetate added exceeds a certain limit, boiling with sodium acetate or addition of caustic ammonia, &c., gives rise to partial separation of the iron.

The quantity of ferric acetate rendered passive by a given quantity of chromic acetate depends upon several circumstances, the most influential of which are the amount of chromic acetate present, the concentration of the liquid, and the temperature at which the acetates act on one another. It increases up to a certain limit with the temperature and the dilution of the solutions, and, so long as the heat is kept below the boiling point, with the duration of the action. Aluminium acetate is acted upon by chromic acetate in the same manner as ferric acetate, excepting that the aluminium is not precipitated, like iron, by boiling with green chromic acetate. The

behaviour of the mixed solutions of aluminic and chromic acetates towards sodium acetate, ammonia, and caustic alkalis, is exactly similar to that which is observed in mixtures of chromic and ferric acetates.  
H. W.

### Molecular Refraction of Methacrylic and Crotonic Acids.

By J. W. BRÜHL (*Ber.*, **14**, 2797—2801). — The constants for methacrylic acid have already been published (this Journal, **38**, 296), and to determine those of crotonic acid, the author has made use of ethyl crotonate (b. p. 139.5—141.5°), which gave the following results:—

$d_{40}^{20}$	A.	B.	$\frac{A-1}{d}$	$P \frac{(A-1)}{d}$
0.9237	1.40881	0.56420	0.4426	50.45

The calculated molecular refraction for ethyl crotonate, supposing it to have the constitutional formula  $\text{Me.CH}:\text{CH.COOC}_2\text{H}_5$ , is 50.06. If the refraction equivalent for the group  $\text{C}_2\text{H}_4$  from 50.45 is deducted, the number 35.57 is obtained; which represents the molecular refraction of liquid crotonic acid. This is practically identical with the molecular refraction of methacrylic acid, viz., 35.07 (*loc. cit.*), thus showing the atom-grouping in these isomerides to be of no influence on the molecular refraction.

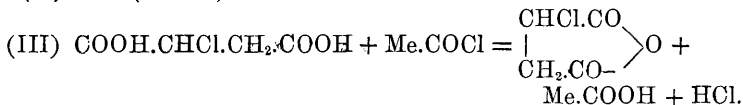
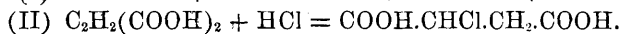
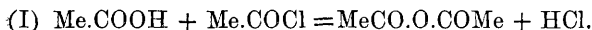
A comparison of these physical constants, in the cases of isobutyric and methacrylic acids, and of ethyl butyrate and crotonate, shows that a removal of two atoms of hydrogen has but little effect on the molecular refraction, yet it increases the refractive index, the density, and the dispersion to a more marked degree.  
P. P. B.

**Preparation of Lactic Acid.** By H. KILIANI (*Ber.*, **15**, 699—701).—The author has extended his researches (cf. this vol., 715) on the preparation of lactic acid, and finds that the best raw material is inverted sugar, and that it is advantageous to substitute sodium for potassium hydroxide; for, apart from its being more economical, it has the effect of removing the greater part of the water entering into the reaction as water of crystallisation in the sodium sulphate formed in the neutralisation. Further, it is unnecessary to neutralise the whole of the alcoholic solution with zinc carbonate, for the zinc salts of the other acids present impede the crystallisation of the zinc lactate; whereas these acids, when set free by the action of the lactic acid on their salts, have no injurious effect. The following is the modification of the author's process:—500 grams raw sugar, 250 grams water, and 10 c.c. sulphuric acid ( $\text{H}_2\text{SO}_4 : \text{H}_2\text{O} = 3:4$ ) are heated for three hours at 50°; to the cooled inverted sugar solution, 400 c.c. of sodium hydroxide ( $\text{NaOH} : \text{H}_2\text{O} = 1:1$ ) are added gradually by 50 c.c. at a time. The mixture rapidly darkens, and the temperature rises almost to boiling if the sodium hydroxide be added in too large quantities. The mixture is then heated at 60—70°, until it gives no reaction with Fehling's solution. Sulphuric acid of the strength mentioned above is then added to neutralise the excess of soda, and the sodium sulphate crystals are separated; the rest of the sulphate is removed by the

addition of 90 per cent. alcohol. The alcoholic solution is drained from the crystals; half of it is neutralised with zinc carbonate, boiled, and filtered when hot into the remaining half. The zinc salt, amounting to 30—40 per cent. of the weight of the sugar, crystallises out on cooling, and, after separation from the mother-liquor, is obtained pure after a single crystallisation. A further crop of zinc lactate may be obtained from the mother-liquor. V. H. V.

**Diamidosuccinic Acid.** By N. LJUBAVIN (*Jour. Russ. Chem. Soc.*, April, 1882, 161).—The compound which the author obtained by acting on glyoxal with ammonium cyanide and subsequently with sulphuric acid, and described (in 1881) as diamidosuccinic acid, is found to be glycocol. B. B.

**Action of Acetic Chloride and Acetic Acid on Fumaric Acid.** By R. ANSCHÜTZ and C. BENNERT (*Ber.*, 15, 640—641).—One of the authors has shown that when fumaric acid is heated with acetic chloride and acetic acid, it gives maleic anhydride. In order to throw light on this change, the authors have subjected the products of the reaction to fractional distillation under reduced pressure, and obtained, besides maleic anhydride, monochlorosuccinic anhydride, the formation of which is explained by the following reactions:—



*Monochlorosuccinic acid*,  $\text{COOH.CHCl.CH}_2\text{COOH}$ , is prepared by heating fumaric acid with a saturated solution of hydrochloric acid in acetic acid; on cooling, the unaltered fumaric acid and part of the monochlorosuccinic acid crystallise out. On evaporating the mother-liquor in a vacuum, the monochlorosuccinic acid (m. p.  $151^\circ$ ) separates. It is easily soluble in water, sparingly soluble in cold acetic acid and chloroform.

*Monochlorosuccinic anhydride*,  $\begin{array}{c} \text{CHCl.CO} \\ | \\ \text{CH}_2\text{CO-} \end{array} \text{O}$ , is obtained from mono-

chlorosuccinic acid and acetic chloride, the crude product of the reaction being distilled under reduced pressure. The anhydride melts between  $38$ — $41^\circ$ , and boils at  $131^\circ$  under pressure of 15 mm., and at  $125^\circ$  under pressure of 12 mm. When monochlorosuccinic anhydride is heated at ordinary pressure, it is decomposed quantitatively into maleic anhydride and hydrochloric acid, thus offering an explanation of the reaction mentioned above.

*Monobromosuccinic Anhydride*,  $\begin{array}{c} \text{CHBr.CO} \\ | \\ \text{CH}_2\text{CO-} \end{array} \text{O}$ . — If fumaric acid is

heated with a saturated solution of hydrobromic in acetic acid, mono-

bromosuccinic acid crystallises out. On heating monobromosuccinic acid with acetic chloride in sealed tubes, and subjecting the product to fractional distillation under reduced pressure, monobromosuccinic anhydride (b. p.  $137^{\circ}$  under pressure of 11 mm.) is obtained. This compound possesses to a remarkable degree the property of superfusion. It can be solidified by the addition of a trace of monochlorosuccinic anhydride; the solid substance melts between  $26-31^{\circ}$ . On distillation at ordinary pressure, monobromosuccinic anhydride is decomposed into hydrobromic acid and maleic anhydride. As maleic, monochloro-, and monobromo-succinic anhydrides yield maleic anhydride by distillation, it would appear that this reaction was general to all the monosubstituted derivatives of succinic acid. V. H. V.

**Itaconic, Citraconic, and Mesaconic Acids.** By R. ANSCHÜTZ (*Ber.*, 14, 2784—2789).—Petri has already shown (*Abstr.*, 1881, 1032) that mesaconic chloride is formed by acting on citraconic anhydride with phosphorus pentachloride; a further study of the fractions of the product of this reaction, distilled under reduced pressure, appears to indicate the presence of a citraconic chloride. Experiments with fumaric chloride and silver oxalate and fumarate have confirmed the results of Perkin (*this Journal*, *Trans.*, 1881, 559).

The investigation of the physical properties of ethyl and methyl citraconates and mesaconates confirm the results of the last-mentioned investigator (*loc. cit.*). The author has not, however, been able to confirm the observation of Swarts (*Bull. de l'Acad. Roy. Belgique* (1873), 36, 64), viz., that chromium mesaconate is formed by saponifying ethyl citraconate with baryta-water.

*Ethyl itaconate* can be obtained by passing hydrochloric acid gas into an alcoholic solution of itaconic acid. This salt, as stated by Swarts (*loc. cit.*), undergoes polymerisation, forming a vitreous mass, which is decomposed by heat.

The author has succeeded in obtaining citraconic anhydride by fractionating the product of the dry distillation of citric acid (*this Journal*, *Abstr.*, 1881, 35) and cooling the fractions to  $-14^{\circ}$ ; those containing this anhydride remain liquid for a lengthened period, whereas the portions containing itaconic anhydride solidify at once. Citraconic anhydride melts at  $+7^{\circ}$ , and appears to resemble maleic and itaconic anhydride in its crystalline form. The examination of the crystals of these two latter compounds shows them to resemble those of succinic anhydride, as shown by the following measurements; they all crystallise in the rhombic system.

Maleic anhydride, $C_2H_2(CO)_2O$	$= a : b : c = 0.64077 : 1 : 0.48066$
Succinic „ $C_2H_4(CO)_2O$	$= a : b : c = 0.59520 : 1 : 0.46168$
Itaconic „ $C_3H_4(CO)_2O$	$= a : b : c = 0.61681 : 1 : 0.45447$

Alcoholic ammonia reacts with ethyl citraconate, forming a substance melting at  $178-179^{\circ}$ , the mother-liquors of which yield crystals (m. p.  $127^{\circ}$ ). P. P. B.

**Molecular Refraction of Methyl and Ethyl Citraconates and Mesaconates.** By J. W. BRÜHL (*Ber.*, 14, 2736—2744).—

Taking the determinations of the respective indices of these two pairs of isomeric salts, as determined by Gladstone (this Journal, Trans., 1881, 558), the author has, by the aid of Cauchy's formula, calculated the respective indices A, for a ray of light of infinite wave-length, and the dispersion B. Further, the density at the temperature of observation, not given by Gladstone, is calculated from the molecular refraction R, for Fraunhofer's line A, by the aid of the following equation:—

$$d = \frac{P(\mu_A - 1)}{R}.$$

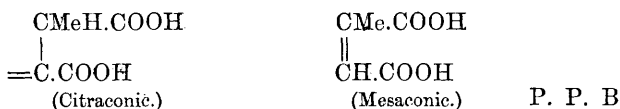
In this way the results contained in the following table have been obtained:—

	$t^\circ$ .	$d$ .	A.	B.	$P\left(\frac{A-1}{d}\right)$ .
Methyl citraconate ..	15.5°	1.1164	1.4339	0.5985	61.41
„ mesaconate ..	16.0	1.1248	1.4373	0.6886	61.43
Ethyl citraconate ....	16.5	1.0480	1.4300	0.5620	76.32
„ mesaconate ....	16.0	1.0500	1.4324	0.6304	76.60

Thus it will be seen that whilst these isomerides possess identical molecular refraction, their dispersive powers are different. Further, by taking the atomic refractions of the elements as determined by the author (this Journal, 38, 295, 685, and 782), and supposing each of the above isomerides to contain two unsaturated carbon-atoms, and also two oxygen-atoms united by double linking, then the calculated molecular refraction of the first pair is 60.92, and of the second pair 75.80, results agreeing fairly well with those deduced from observation.

These results confirm the conclusion of the author, viz., that the molecular refraction is independent of the arrangement of the atoms in a molecule, but indicates the degree of saturation of these atoms. Thus the identity of the molecular refractions of these isomerides indicates the presence in mesaconic and citraconic acids of a pair of unsaturated carbon-atoms, or of the group C—C, and that the

isomerism of these acids cannot be explained by the formulæ:—



**Dextro-tartaric Acid and Lævo-malic Acid.** By R. ANSCHÜTZ (*Ber.*, 14, 2789—2792).—By the method already described (this Journal, 38, 876), the following salts and derivatives of dextro-tartaric acid have been prepared:—

	Melting point.	Boiling point at 23 mm.	Boiling point at ordinary pressure.
Isopropyl dextrotartrate .....	liquid	165°	275°
Isobutyl           ".....	68°	197	323—325°
Diacetmethyl dextrotartrate ..	103·0°	—	—
Diacetethyl           " ..	66·5	—	291—292°
Diacetpropyl       " ..	31·0	—	313°
Diacetisobutyl     " ..	liquid	—	322—326°
Dibenzoic methyl dextrotartrate	132°	—	decomposes
Dibenzoic ethyl       " ..	liquid	—	"
Dibenzoic isobutyl   " ..	liquid	—	"

Similar attempts to prepare the ethereal malonates have failed. The acetic derivatives may be easily obtained; their boiling points are about 40° higher than those of the corresponding fumarates.

*Acetomalic anhydride*,  $C_6H_6O_5$ , is prepared by acting on malic acid with acetic chloride, and fractionating the product under reduced pressure. Prepared in this way, it is a viscous liquid, solidifying to a crystalline mass, melting at 53—54°, and boiling at 160—162° under a pressure of 14 mm. When heated to boiling under ordinary pressure, it forms maleic anhydride (*vide* Perkin, this Journal, Trans., 1881, 562), the quantity formed being some 70 per cent. of the theoretical yield.

The author confirms the statement of Perkin (*loc. cit.*, 560), viz., that acetic chloride containing acetic acid converts fumaric acid into maleic anhydride.

P. P. B.

**Synthesis of so-called Alkyl Disulphoxides.** By R. OTTO (*Ber.*, 15, 121—132).—The method employed by the author for the synthesis of sulphones, viz., the action of haloid paraffin derivatives on sulphinates, seemed capable of being applied to the synthesis of the so-called disulphoxides,  $R_2S_2O_2$ , by substituting a thioalkylsulphonate for the sulphinate.

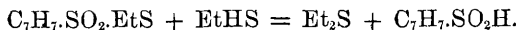
*Ethyl disulphoxide* or *ethyl thioethylsulphonate*,  $EtSO_2.EtS$ . Ethyl disulphide is converted into ethylsulphonic acid by the action of nitric acid, and then into the corresponding chloride by treatment with phosphorus pentachloride in the usual way. When purified by fractional distillation, the chloride is a transparent highly refractive liquid (b. p. 171°), having a pungent odour, closely resembling that of mustard oil. Potassium thioethylsulphonate,  $EtSO_2.KS$ , is easily prepared from this chloride by adding it gradually to a moderately concentrated aqueous solution of potassium sulphide, evaporating to dryness, and treating the residue with boiling absolute alcohol, which dissolves the thioethylsulphonate. This alcoholic solution may be at once used for the preparation of ethyl thioethylsulphonate by adding ethyl bromide in quantity corresponding to the sulphonic chloride originally taken, and boiling the mixture for some hours with reflux condenser: the alcohol is then distilled off and water added, which causes the separa-



tion of an oil consisting of ethyl thioethylsulphonate mixed with some ethyl bisulphide and ethylsulphonate. On boiling the mixture of oil and water for some time with reflux condenser, the ethylsulphonate alone is saponified, and on subsequently distilling in a current of steam the more volatile ethyl bisulphide passes over first, and is succeeded by the ethyl thioethylsulphonate, which is far less volatile, so that the two can readily be separated. Another mode of separation is to agitate the mixture—after saponification of the ethylsulphonate in the manner above described—with light petroleum, which dissolves the ethyl bisulphide and leaves the thioethylsulphonate. Ethyl thioethylsulphonate prepared in this way is a colourless oil soluble in alcohol and ether, and volatilises unchanged with water vapour. When heated alone, it distils between  $130^{\circ}$  and  $140^{\circ}$ , but is decomposed at the same time. It is identical with Lowig and Wiedmann's "ethyl disulphoxide" obtained by the action of nitric acid on mercaptan (*Ann. Chem. Phys.*, **49**, 323). It is not attacked when heated with water at  $120^{\circ}$  in sealed tubes, but when warmed with potash solution it is decomposed, ethyl bisulphide and potassium ethylsulphinate being formed. The alcoholic solution treated with zinc and sulphuric acids yields mercaptan, and with zinc-dust it gives zinc mercaptide and ethylsulphinate, together with some free mercaptan.

*Ethyl thiobenzenesulphonate*,  $\text{PhSO}_2\cdot\text{EtS}$  (Abstr., 1880, 812), prepared by the action of ethyl bromide on potassium thiobenzenesulphonate, is a colourless oil, which cannot be distilled without decomposition; it closely resembles the other so-called disulphoxides in properties. The action of zinc and sulphuric acid on the alcoholic solution produces ethylmercaptan and phenylmercaptan, whilst with zinc-dust it yields zinc mercaptide and benzenesulphinate with some free mercaptan.

*Ethyl thioparatoluenesulphonate*,  $\text{C}_7\text{H}_7\text{SO}_2\cdot\text{EtS}$ , prepared in a similar manner to the above, is a colourless transparent somewhat viscid oil, which on exposure to a moist atmosphere, becomes turbid and soon solidifies to a crystalline mass, which again becomes liquid and transparent in a dry atmosphere. It does not volatilise to any extent in a current of water vapour, but in other respects closely resembles the corresponding benzene compound. When heated with potash solution, it is decomposed, yielding ethyl bisulphide and potassium paratoluenesulphinate. When boiled with mercaptan, it forms ethyl bisulphide and paratoluenesulphinic acid as follows:—



Ethylene bromide reacts with the thiosulphonates as easily as ethyl bromide does. The author is engaged in investigating the nature of the new compounds thus produced.

In conclusion, the author gives Köbig and Fock's measurements of the crystals of benzene- and paratoluene-disulphoxides.

Phenyl thiobenzenesulphonate crystallises in short thick prisms belonging to the monoclinic system—

$$a : b : c = 1.4460 : 1 : 1.4706.$$

Observed forms, 110, 001, 010,  $\bar{1}11$ ,  $\bar{1}01$ .

Optical axis parallel to the plane of symmetry.

Tolyl parathiotoluenesulphonate crystallises in thick hexagonal plates belonging to the monoclinic system—

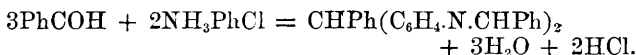
$$a : b : c = 0.4463 : 1 : 1.0151.$$

Observed forms, 001, 110, 010, and occasionally 111 and  $\bar{1}11$ .

Cleavage perfect in the plane of symmetry.

C. E. G.

**Condensation Products of Aromatic Bases.** By O. FISCHER (*Ber.*, 15, 676—683).—The author has already shown that by the action of aldehydes on the hydrochlorides of primary amines, compounds are formed derived from three molecules of the aldehyde and two molecules of the base, thus:



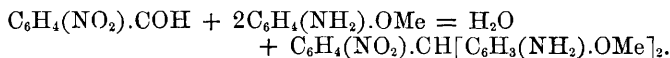
By substituting the sulphate or phosphate of the base for the hydrochloride, the aldehyde and aniline will react, molecule for molecule, with formation of diamidotriphenylmethane. In like manner derivatives of benzaldehyde and aniline give derivatives of diamidotriphenylmethane. Thus *paranitrobenzaldehyde* and aniline sulphate, when heated with zinc chloride, give *paranitrodiamidotriphenylmethane*. This substance forms citron-yellow flocculæ, easily soluble in benzene, toluene, &c. Like all the triphenylmethane derivatives, it combines with benzene and toluene to form crystalline compounds. Its hydrochloride crystallises in silky glistening needles, which, when heated to 100° in a current of hydrogen, decompose into the base and hydrochloric acid; the sulphate crystallises in star-shaped grouped needles. *Paranitrodiamidotriphenyl* gives *paraleucaniline* on reduction with tin and hydrochloric acid.

*Paranitrobenzaldehyde* and *orthotoluidine* give an analogous compound.

By reduction with tin and hydrochloric acid, it forms a leucaniline, which the author names *diortholeucaniline*; its salts resemble those of leucaniline, but its hydrochloride is more soluble in concentrated hydrochloric acid than that of leucaniline; the free base crystallises in small colourless prisms or needles, which rapidly turn pink in the air. The magenta obtained by oxidation from *diortholeucaniline* is of a more intense blue than *pararosaniline*.

The author draws attention to the fact that on comparison of the three known rosanilines, the entrance of the methyl group into the benzene nuclei of *pararosaniline* increases the tint of blue, but not to such an extent as the entrance of the methyl group into the amido-residue.

*Paranitrobenzaldehyde* and *orthoanisidine* react in a similar way to form a substance which separates out in golden flocks. It crystallises from benzene in glistening needles (m. p. 108°) of formula  $\text{C}_{21}\text{H}_{21}\text{N}_3\text{O}_4$  +  $\text{C}_6\text{H}_6$ ; the reaction is as follows:—



On oxidation with chloranil, this nitroleuco-base gives a golden-

green dyestuff; on reduction with tin and hydrochloric acid, it forms leucanisidine,  $C_{21}H_{23}N_3O_2$ , crystallising in plates or tables (m. p.  $183^\circ$ ), which rapidly turn red in the air. The hydrochloride of leucanisidine is very soluble in concentrated hydrochloric acid; the platinichloride forms a golden crystalline mass; on heating the hydrochloride to  $130^\circ$ , it forms rosanisidine hydrochloride, which dissolves in alcohol and water to form red solutions, with a strong blue fluorescence.

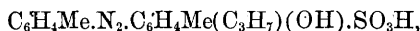
*Orthonitrobenzaldehyde* and *dimethylaniline* react to form a nitroleuco-base, which crystallises in golden prisms (m. p.  $155^\circ$ ), sparingly soluble in cold water and alcohol. On reduction of the nitroleuco-base with tin and hydrochloric acid, a tetramethyltriamidotriphenylmethane,  $C_{23}H_{27}N_3$ , is obtained crystallising in star-shaped prisms (m. p.  $126^\circ$ ), which give on oxidation a reddish-violet dyestuff.

V. H. V.

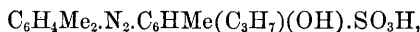
#### Action of Diazo-Compounds on $\alpha$ -Thymolsulphonic Acid.

By J. H. STEBBINS (*Ber.*, **14**, 2793—2797).—*Sodium azobenzenethymolsulphonate*,  $Ph.N_2.C_6HMe(C_3H_7)(OH).SO_3Na$ , is obtained by acting on an alkaline solution of  $\alpha$ -thymolsulphonic acid with diazobenzene chloride. It crystallises from hot water, by which it is partially decomposed, in yellow needles, possessing tinctorial power, and imparting a yellow colour to wool. The barium salt is obtained as a yellow precipitate by adding barium chloride to a solution of the sodium salt. It is sparingly soluble in hot water, but soluble in aqueous alcohol. The free acid is obtained as a red precipitate by decomposing the sodium salt with hydrochloric acid. It crystallises from hot water in small yellow six-sided prisms, melting with decomposition at  $215.75^\circ$ .

In a similar manner parazotoluene- $\alpha$ -thymolsulphonic acid,



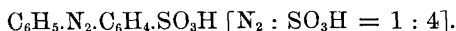
and azoxylene- $\alpha$ -thymolsulphonic acid,



have been prepared by the action of paradiazotoluene chloride and diazoxylene chloride respectively on an alkaline solution of  $\alpha$ -thymolsulphonic acid. These compounds resemble the above, impart a yellow colour to wool, and are decomposed on being boiled with water. The solubility of these compounds decreases with increase in molecular weight.

P. P. B.

**Azobenzenesulphonic Acids.** By J. V. JANOVSKY (*Monatsh. Chem.*, **3**, 237—248).—The azobenzenemonosulphonic acid which Griess obtained by the action of pyrosulphuric acid on azobenzene (*Annalen*, **131**, 89), is converted by reduction with tin and hydrochloric acid into paramidobenzenesulphonic or sulphanilic acid, and must therefore consist of azobenzeneparasulphonic acid,



The corresponding *chloride*,  $C_6H_5.N_2.C_6H_4.SO_2Cl$ , obtained by the action of  $PCl_5$  on the sodium salt, crystallises in tufts of orange-red

needles. It is partly decomposed by heat, but a portion sublimes in golden-yellow needles; from benzene it crystallises in thin laminae, m. p.  $82^{\circ}$ .

*Azobenzenedisulphonic Acids*,  $C_{12}H_8N_2(SO_3H)_2$ .—The author prepares these acids by mixing 1 pt. azobenzene with 4 pts. crystallised pyrosulphuric acid, heating the mass at  $150$ — $160^{\circ}$  for half an hour, then leaving it to cool, and diluting with 1— $1\frac{1}{2}$  vol. water, whereupon it becomes very hot, and on cooling solidifies to a magma, which must be collected on a platinum funnel, and freed from mother-liquor as completely as possible by aspiration. From the mother-liquor, a further portion of the acids may be obtained by converting them into barium salts.

The mass on the funnel contains three disulphonic acids, and on dissolving it in a small quantity of water, a certain portion of monosulphonic acid is usually left behind. The solution contains the disulphonic acids, and when left to evaporate, often deposits concentric groups of crystals consisting of the least soluble of the three. Two of these acids may be separated by conversion into barium, potassium, or lead salts, the salts of one of them (Limpricht's  $\alpha$ -acid) being but slightly soluble in water, while those of the second ( $\beta$ ) are easily soluble. On spontaneous evaporation of the strongly acid mother-liquor obtained in the preparation of the crude acids, the third acid ( $\gamma$ ) separates in granular crystals convertible into distinct prisms by recrystallisation. The separation of the acids may also be effected by concentrating the solution as far as possible, and adding fuming hydrochloric acid, which throws down the  $\beta$ -acid. The aqueous solution of this acid yields fine broad laminae, having the composition,

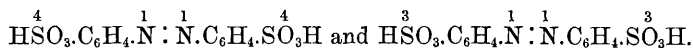


The  $\alpha$ -acid, already described by the author (p. 48 of this volume), agrees with Limpricht's  $\alpha$ -acid (p. 517).

To determine the orientation in the three acids obtained as above, they were reduced by tin and hydrochloric acid to amidobenzenesulphonic acids, the dissolved tin was precipitated by hydrogen sulphide, and the hydrochloric acid evaporated, whereupon there remained a mass of slightly coloured crystals. This residue, in case the two sulpho-groups are symmetrically situated in the two benzene-nuclei, can consist only of (1 : 2), (1 : 3), or (1 : 4) amidobenzenesulphonic acid; but if the two sulpho-groups are in the same nucleus, it may consist of six amidobenzenedisulphonic acids, in which the two  $SO_3H$ -groups occupy with regard to the  $NH_2$  in 1, the positions 2 : 3, 2 : 4, 2 : 5, 2 : 6, 3 : 4, 3 : 5. This residue was treated with alcohol (92 per cent.), which left undissolved a faintly lilac-coloured mass, A; and the filtrate, B, after concentration over the water-bath, was treated with water and crystallised over sulphuric acid.

The residue A treated with fuming hydrochloric acid, was separated into two acids, and on recrystallisation from water (1 : 70), a sparingly soluble portion remained, which, after several crystallisations from water, yielded sulphanilic acid [1 : 4], while the mother-liquor deposited, first a small additional quantity of this acid, and then small lilac-coloured prismatic crystals of metamidobenzenesulphonic acid

[ $\text{NH}_2 : \text{SO}_3\text{H} = 1 : 3$ ]. Hence it follows that by direct sulphonation of azo-benzene, two sulpho-acids are obtained, having the sulpho-groups in different benzene-nuclei, and represented by the formulæ—



The more soluble *para*-acid crystallises by spontaneous evaporation in large ruby-red needles containing 3 mol.  $\text{H}_2\text{O}$ ; otherwise in concentrically grouped reddish-yellow needles containing  $2\text{H}_2\text{O}$ . The corresponding *sulphochloride* was found by the author to differ somewhat in its properties from that described by Limpricht. When prepared from the sodium salt and recrystallised from chloroform, it forms dark red feathery crystals melting at  $170^\circ$ ; from ether it separates in compressed pyramidal forms; from benzene in long ruby-red needles. *Potassium azobenzene-p-sulphonate* forms yellowish-red concentrically grouped laminæ; the *barium salt* concentric or warty groups of needles.

The *meta*-acid, purified by fractional crystallisation, crystallises in yellow-red laminæ, sparingly soluble in water, easily in strong hydrochloric acid, and appearing under the microscope to consist of swallow-tailed twins. The potassium and barium salts are more soluble than those of the *para*-acid. The *sulphochloride* crystallises from ether in needles, from chloroform in broader prisms melting at  $143^\circ$ .

The third azobenzenesulphonic acid, which often separates by spontaneous evaporation from the mother-liquor of the other two after dilution with water, has not yet been obtained quite pure, but it yields by reduction with tin and hydrochloric acid an acid closely resembling the so-called disulphanilic acid,  $\text{C}_6\text{H}_3(\text{NH}_2)(\overset{2}{\text{SO}_3\text{H}})\cdot\overset{4}{\text{SO}_3\text{H}}$ . Hence it may be inferred that the azo-acid has its two sulpho-groups in the same benzene-nucleus and in the *meta*-position with regard to each other, as represented by the formula  $\text{C}_6\text{H}_5\cdot\overset{1}{\text{N}}_2\cdot\text{C}_6\text{H}_3(\overset{2}{\text{SO}_3\text{H}})(\overset{4}{\text{SO}_3\text{H}})$ .

*Substitution-products of Azobenzenemonosulphonic Acid.*—The mononitro-acid,  $\text{C}_{12}\text{H}_8(\text{NO}_2)(\text{SO}_3\text{H})\text{N}_2$ , is obtained by adding the monosulpho-acid to ten times its quantity of strong nitric acid (1.48), warming the mixture for a little while, and expelling the excess of nitric acid; when all the sulpho-acid is nitrated, the liquid is no longer clouded by water. The evaporated liquid is a yellow syrup, which crystallises over sulphuric acid in hydrated plates and nodules. The process appears indeed to yield two acids, only one of which has yet been studied. This acid and its salts detonate very strongly when heated. The *barium salt*  $(\text{C}_{12}\text{H}_8(\text{NO}_2)\cdot\text{SO}_3)_2\text{Ba} + 6\text{H}_2\text{O}$ , is sparingly soluble, and crystallises in stellate groups of microscopic needles. The *silver salt*, also sparingly soluble, separates from hot water in yellow anhydrous microscopic crystals, which detonate very strongly when heated. The *potassium salt* crystallises in concentric groups of sparingly soluble yellow needles.

The mother-liquors of the barium and silver salts have a deep yellow-red colour, and on spontaneous evaporation leave crystals essentially different from those above described, indicating the exist-

ence of a second nitro-acid, which the author proposes to examine further.

By fusing azobenzenemonosulphonic acid with potassium cyanide, a brown oily distillate is obtained, which appears to be a nitrate of azobenzene-carboxylic acid, and when saponified or boiled with hydrochloric acid, yields an acid crystallising in laminæ. H. W.

**Paraxylenol.** By V. OLIVERI (*Gazzetta*, 1882, 161—167).—The paraxylenol used in the preparation of the following derivatives was obtained, according to Jacobsen's directions (this Journal, **32**, 600), from the portion of commercial xylene not dissolved by ordinary sulphuric acid, and passed over on distillation between 137° and 139°.

*Nitroso-paraxylenol*,  $C_6H_4Me_2(NO).OH$ , is prepared by mixing a solution of *p*-xylenol in caustic potash with an aqueous solution of potassium nitrite, cooling the mixture to 0°, decomposing it with dilute acetic acid, and again cooling the liquid. A copious precipitate is thus obtained, which becomes resinous if left in the liquid, but may be purified by collecting it on a cloth, pressing it between paper, and repeatedly crystallising it from very dilute alcohol. It forms long well-defined reddish needles, soluble in alcohol, ether, and benzene, nearly insoluble in water, melting, with decomposition, at 160—165°.

*The three Isomeric Nitro-paraxylenols*,  $C_6H_4Me_2(NO_2).OH$ .—The  $\alpha$ -modification, formed by dissolving the nitroso-compound in dilute aqueous potash and oxidising with potassium ferricyanide, crystallises in very slender, well-defined, nearly colourless needles, soluble in alcohol, ether, and boiling water, very slightly in cold water, to which it imparts a fine canary-yellow colour; melts at 115°. The  $\beta$ -modification, obtained by treating *p*-xylenol, dissolved in glacial acetic acid, with fuming nitric acid, is a yellowish fragrant oil, boiling with partial decomposition at 236°. Its potassium salt, prepared by dissolving the nitroxylenol in excess of aqueous potash, evaporating, leaving the residue for some time exposed to the air, and then treating it with absolute alcohol to separate potassium carbonate formed at the same time, is a red-brown mass very soluble in water and in alcohol. The *barium salt*,  $(C_6H_4NO_2.O)_2Ba$ , obtained from the potassium salt by precipitation with barium chloride, forms shining, deep purple, anhydrous scales, soluble in boiling water, very slightly also in cold water. The  $\gamma$ -modification is obtained by the action of nitric acid on *p*-xylenol-sulphonic acid dissolved in water, and crystallises in splendid canary-yellow scales, melting at 89°, slightly soluble in water, freely in alcohol and ether. Its *potassium salt*,  $C_6H_4(NO_2).OK + H_2O$ , crystallises in long flexible orange-yellow needles which give off their water at 130°, acquiring a scarlet colour, and explode with great violence at 260°. It is less soluble than the potassium salt of  $\beta$ -nitro-*p*-xylenol. The *barium salt*,  $(C_6H_4NO_2.O)_2Ba + H_2O$ , crystallises in canary-yellow scales which give off their water at 130°, assuming an orange-yellow colour.

*Paraxylenol-carboxylic acid*,  $C_6H_4Me_2(OH).COOH$ , is prepared by passing a stream of carbonic anhydride over *p*-xylenol in a retort containing pellets of sodium and heated to 180°, the action being kept up for 12 hours, and sodium added from time to time. The unaltered sodium

is then removed by water, gradually added, which dissolves the product; the liquid is filtered and exhausted with ether; the ethereal solution is treated with sodium carbonate to dissolve out the acid produced; the solution of the sodium salt is treated with hydrochloric acid, which throws down the *p*-xylene-carboxylic acid; and the precipitate is pressed between paper, purified with animal charcoal, and crystallised from a mixture of alcohol and water.

Paraxylene-carboxylic acid thus obtained crystallises in long colourless silky needles, soluble in alcohol and ether, slightly soluble in water. The aqueous solution is coloured violet by ferric salts. The crystals melt at 137°. The *barium salt*,  $(C_8H_9O_3)_2Ba + 4H_2O$ , forms very small colourless needles very soluble in water.

Wroblewsky (*Zeitschr. f. Chem.*, 1868, p. 252), by treating xyleneol from commercial xylene with sodium and carbonic anhydride, obtained a xylene-carboxylic acid, different from that here described, inasmuch as it melted at 155° and formed a barium salt differing in its amount of crystal-water from that of the acid prepared from *p*-xyleneol.

H. W.

### Synthesis by means of Anhydrous Magnesium Chloride.

By G. MAZZARA (*Gazzetta*, 1882, 167—168).—The author, after noticing various syntheses of organic compounds by means of dehydrating agents, such as strong hydrochloric and sulphuric acid, phosphoric anhydride and zinc chloride, proceeds to describe the formation of certain phenols by the aid of anhydrous magnesium chloride, viz.: (1.) *Isobutylphenol*,  $CHMe_2.CH_2.C_6H_4.OH$ , from isobutyl alcohol and phenol, together with another substance insoluble in potash; probably the corresponding isobutylic ether. (2.) *Propylmetacresol*,  $C_3H_7.C_6H_3Me.OH$ , from propyl alcohol and metacresol: boils at 230—235°; gives no coloration with ferric salts. At the same time there is formed the corresponding propylic ether,  $C_3H_7.C_6H_3Me.OOC_3H_7$ , which boils at a somewhat higher temperature. (3.) *Isopropylmetacresol*,  $CHMe_2.C_6H_3Me.OH$  (b. p. 225—230°), is formed in like manner together with its isopropylic ether. The phenol boils at 225—230°.

H. W.

**Action of Acid Chlorides and Bromides on Quinones.** By H. SCHULZ (*Ber.*, 15, 652—659).—By the action of acid chlorides and bromides on quinone, haloïd derivatives of ethereal salts of quinol (which have previously been studied by Wichelhaus and others) are formed thus:  $C_6H_4O_2 + 2AcCl = C_6H_4(OAc)_2 + Cl_2 = C_6H_3Cl(OAc)_2 + HCl$  and  $C_6H_3Cl(OAc)_2 + Cl_2 = C_6H_2Cl_2(OAc)_2 + HCl$ . Thus quinone and acetic chloride yield mono- and di-chloroquinyl acetate, and quinone and acetic bromide yield mono- and di-bromoquinyl acetate; and similarly monochloroquinone and acetic bromide yield chlorbromoquinyl acetate.

On heating thymoquinone and acetic chloride in sealed tubes, monochlorothymyl diacetate,  $C_8HClMePr(OAc)_2$ , is obtained, crystallising in rhombic leaflets (m. p. 87°), easily soluble in alcohol and ether; the corresponding monobromothymyl diacetate crystallises in rhombohedrons (m. p. 91°), soluble in acetic acid, sparingly soluble in petroleum. Benzoic chloride behaves like acetic chloride; with thymoquinone it yields mono- and di-chlorothymyl di-benzoate,  $C_8HClMePr(OBz)_2$  and

$\text{CCl}_2\text{MePr}(\text{OBz})_2$ ; the former crystallises in white needles (m. p.  $191^\circ$ ). The author proposes to carry on further experiments on these compounds. V. H. V.

**Oxidation of Pyrogallol in presence of Free Acid.** By P. DE CLERMONT and P. CHAUTARD (*Compt. rend.*, **94**, 1189—1192).—When pyrogallol is oxidised in presence of free acid by silver nitrate, chromic acid, or potassium permanganate, the reaction is complex, purpurogallin being the principal product. When the oxidising agent was potassium permanganate mixed with sulphuric acid, the authors were able to isolate, in addition to purpurogallin, pyrogalloquinone, and a third substance, the composition of which has not been determined, but which forms small needles and transparent prismatic tables with a silvery lustre. Analysis of carefully purified purpurogallin, of the barium and sodium salts, and of its acetyl-, ethyl-, bromo-, and nitro-derivatives, proves that its true formula is  $\text{C}_{20}\text{H}_{16}\text{O}_9$ , as found by Gerard, and not  $\text{C}_{18}\text{H}_{14}\text{O}_9$ , as found by Wichelhaus. Heated with hydriodic acid in sealed tubes, purpurogallin yields a hydrocarbon containing  $\text{C}_{10}$ , and probably higher homologues containing  $\text{C}_{10n}$ . C. H. B.

**Preparation of Aromatic Ethereal Salts of Phosphoric Acid.** By A. WEBER and A. HEIM (*Ber.*, **15**, 639—640).—The aromatic ethereal salts of phosphoric acid can easily be prepared by the action of phosphorus oxychloride on the phenols. The authors have thus obtained triphenyl, tri- $\beta$ -naphthyl and tricresyl phosphate from the corresponding phenols. V. H. V.

**Derivatives of Umbelliferone.** By E. POSEN (*Ber.*, **14**, 2744—2747).—*Umbelliferone*,  $\text{OH} \cdot \text{C}_6\text{H}_3 < \text{CH} : \text{CH} > \text{CO}$ , may be obtained from acetumbelliferone, described by Ziemann and Lewy (*Abstr.*, 1878, 424), also by Ziemann and Riemer (*ibid.*, 1879, 721), by heating this compound for a few minutes at  $50^\circ$  with a dilute aqueous potash solution.

*Umbellic acid*,  $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{CH} : \text{CH} \cdot \text{COOH}$ , is obtained by heating umbelliferone with potash at  $70^\circ$ , and decomposing the product with hydrochloric acid. It is soluble in warm water and in alcohol, but insoluble in ether and benzene. It has not been obtained crystalline, and when dry forms a yellowish powder: it decomposes at  $260^\circ$ . The salts with the alkalis and alkaline earths are soluble, the lead and copper salts are insoluble. It reduces ammoniacal solutions of silver salts.

*Tribromumbelliferone*,  $\text{OH} \cdot \text{C}_6\text{Br}_3 < \text{CH} : \text{CH} > \text{CO}$ , is obtained by adding bromine to a hot aqueous solution of umbelliferone. It is insoluble in water, but soluble in alcohol, from which it crystallises in small white needles, m. p.  $196^\circ$ . Its solutions give a greenish-yellow fluorescence. It is decomposed by alkalis.

*Trinitroumbelliferone*,  $\text{OH} \cdot \text{C}_6(\text{NO}_2)_3 : (\text{C}_3\text{H}_2\text{O}_2)$ , is obtained by adding umbelliferone carefully to a mixture of concentrated nitric and sulphuric acids, and pouring the product into water. It is soluble in the



ordinary solvents, and crystallises from benzene in yellow needles, united in rosettes which contain 1 mol. of benzene; this is expelled at 100°, and it then melts at 216°. Its solutions are decomposed by alkalis.

P. P. B.

**Orthonitrobenzaldehyde.** By P. FRIEDLÄNDER and R. HENRIQUES (*Ber.*, 14, 2801—2805).—This compound is formed by the oxidation of orthonitrocinnamic acid in cold alkaline solution with dilute solution of potassium permanganate, and can be obtained from the filtrate from the manganese dioxide, by acidifying it and extracting with ether. A better method of preparation is a modification of that described by Friedländer for preparing paranitrobenzaldehyde (this vol., 401). According to this method, ethyl orthonitrocinnamate dissolved in concentrated nitric acid is treated with small quantities of sodium nitrite, and after standing for some time the product is poured into water. The aldehyde separates out as an oil, and after being washed with water, is purified by distillation in a current of steam.

The aldehyde prepared in this way has essentially the properties attributed to it by Gabriel and Meyer (*Abstr.*, 1881, 729; and this vol., 188). It is soluble in the ordinary solvents, and crystallises in light yellow needles (m. p. 46°). It unites with sodium hydrogen sulphite to form a compound easily soluble in water. By oxidation, it is converted into orthonitrobenzoic acid, and by concentrated soda-solution, is converted into orthonitrobenzyl alcohol, which crystallises in yellowish needles (m. p. 74°). This compound has already been described by Jaffé, who observed its formation by the passage of orthonitrotoluene through the animal organism.

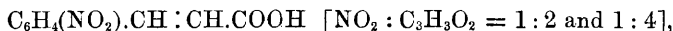
The authors confirm the observation of Rudolph on the action of nascent hydrogen on orthonitrobenzaldehyde (*Abstr.*, 1880, 469).

P. P. B.

**Synthesis of Parapropylbenzoic Acid.** By R. MEYER and E. MÜLLER (*Ber.*, 15, 698—699).—The author has synthesised parnormalpropylbenzoic acid by the action of moist carbonic acid on sodium and parabromopropylbenzene. By the oxidation of synthetical cuminic acid with potassium permanganate, besides terephthalic acid, hydroxypropylbenzoic acid,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$ , is also formed.

V. H. V.

**Derivatives of Para- and Ortho-nitrocinnamic Acid.** By C. L. MÜLLER (*Annalen*, 212, 122—149).—These acids,



are best prepared by adding finely pulverised cinnamic acid to nitric acid of sp. gr. 1.48, mixing the pasty mass with 10 vols. iced water, decanting the milky liquid, washing the residue with water, and drying it at a gentle heat on earthenware slabs; and they are most readily separated from one another by converting them into the corresponding ethyl-salts, which is effected by drenching the crude product with alcohol of 93 per cent., and heating the mixture in an apparatus with reversed condenser in a rapid stream of hydrogen. The whole then dissolves to a yellow liquid, which solidifies to a crystalline pulp, to be

purified by draining off the alcoholic liquid, and washing first with cold alcohol, then with dilute aqueous ammonia. In this manner the greater part of the ethylic para-nitrocinnamate is obtained in yellowish needles melting at  $137^{\circ}$ ; and the mother-liquor freed from part of the alcohol by distillation, and then left to evaporate, yields the ortho-ether, in thin yellow rhombic crystals melting at  $42^{\circ}$ , together with a white precipitate of orthonitrocinnamic acid (m. p.  $232^{\circ}$ ), due either to imperfect etherification or to partial decomposition of the ether by the water present. The acid and ether thus obtained are best separated by evaporating off the alcohol, treating the residue with carbon bisulphide, which dissolves the ether, especially with the aid of heat, leaving the free acid undissolved. About a third of the orthonitrocinnamic acid is thus obtained in the free state, the rest as ethylic ether.

The free acids may be prepared from the ethers by boiling the latter in the state of fine powder, with a somewhat concentrated solution of sodium carbonate, and purified by recrystallisation from hot alcohol. Para-nitrocinnamic acid is thus obtained in the form of thin, yellowish, highly lustrous needles or laminæ, which turn brown at  $260^{\circ}$ , and melt at about  $276^{\circ}$ . The ortho-acid forms an extremely loose white mass, consisting of very thin felted needles, which begin to turn brown at  $225^{\circ}$ , and melt at  $232^{\circ}$ .

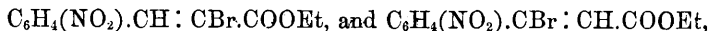
*Action of Bromine on the two Ethylic Nitrocinnamates.*—The two nitrocinnamic acids are but slowly attacked by bromine, the combination not being complete even when they are left for a week in a shallow glass vessel, under a bell-jar, together with bromine; but with the ethers combination takes place much more readily. To prepare these bromine-compounds, the nitrocinnamic ether (20 g.) dissolved in 300 g. carbon bisulphide is heated in a reflux apparatus with 15 g. bromine, the liquid being boiled till it becomes colourless, after which part of the carbon bisulphide is distilled off, and the rest left to evaporate, the bromide of the ethylic nitrocinnamate (or ethylic nitrophenyldibromopropionate) then remaining in crystals.

The para-compound,  $\text{C}_6\text{H}_4(\text{NO}_2)(\text{CHBr}.\text{CHBr}.\text{COOEt})$  thus prepared separates in tufts of yellowish crystals, having an intensely disagreeable odour; it dissolves easily on warming in alcohol and carbon bisulphide, and separates from the hot saturated solutions in fine monoclinic prisms, perfectly colourless and inodorous, and melting at  $110$ — $111^{\circ}$ . It dissolves readily also in ether, light petroleum, and chloroform. The ortho-compound forms faintly yellow monoclinic crystals, very easily soluble in alcohol, ether, light petroleum, chloroform, and carbon bisulphide, and melting at  $71^{\circ}$ .

*Action of Alcoholic Potash on Ethylic Paranitrophenyldibromopionate.*—By acting on 1 mol. of this ether with 2 mols. potassium hydroxide dissolved in alcohol, the author expected to obtain nitrobromocinnamic acid, according to the equation—



Instead of this, however, a mixture of two isomeric ethyl paranitrobromocinnamates,



was obtained, together with potassium bromide and other products. The two *p*-nitrobromocinnamic ethers are separated from the potassium bromide by agitating the crystalline product with ether, and are deposited on distilling off part of the ether, the one ( $\alpha$ ) in large prisms melting at  $63^\circ$ ; the other ( $\beta$ ) in small slender needles melting at  $93^\circ$ . The two may be separated by picking out the large crystals as completely as possible, and dissolving the remainder in about 80 pts. of hot alcohol, which on cooling deposits the  $\beta$ -compound in needles, leaving in solution the rest of the  $\alpha$ -compound, which may be purified by repeated crystallisation.

*Ethylic  $\alpha$ -paranitrophenylbromocinnamate* (m. p.  $63^\circ$ ) crystallises in thin transparent rhombic prisms, having a yellow colour and strong lustre; dissolves readily in alcohol, ether, chloroform, and carbon bisulphide.—The  $\beta$ -compound (m. p.  $93^\circ$ ) crystallises in very slender, slightly yellowish needles, having a faint silky lustre; it is somewhat less soluble in cold alcohol than the  $\alpha$ -compound, easily soluble in ether, chloroform, and carbon bisulphide.

The potassium salt obtained in the above reaction, after being freed by ether from the admixed ethylic nitrobromocinnamates, was dissolved in water and decomposed by sulphuric acid, whereby a white precipitate was formed, which, after washing and drying, melted at  $142$ – $150^\circ$ , and gave by analysis numbers indicating a mixture of nitrobromocinnamic and nitrophenylpropionic acid,  $\text{C}_6\text{H}_4(\text{NO}_2).\text{C}:\text{C}.\text{COOH}$ , but on distilling the substance in a current of steam, in the expectation that the nitrophenylpropionic acid would pass over, just as Glaser's phenylpropionic acid does when similarly treated, there was obtained, instead of the expected acid, a neutral body, having a peculiar aromatic odour extremely pungent in ethereal solution, and the composition of *nitrophenylacetylene*,  $\text{C}_6\text{H}_4(\text{NO}_2).\text{C}:\text{CH}$ , formed from nitrophenylpropionic acid by separation of  $\text{CO}_2$ . This nitro-compound melts at  $149^\circ$ , dissolves readily in alcohol, ether, chloroform, and carbon bisulphide, very sparingly in water, and exhibits the property, characteristic of acetylene, of forming metallic derivatives; the copper-compound has a deep red colour; the silver-compound is greenish-yellow.

In the distillation of the above-mentioned mixture of acids with steam, a portion dissolved in the boiling water; and on filtering, an insoluble residue was obtained, which, after washing with a little hot water, and drying over sulphuric acid, melted at  $205^\circ$ , and gave by analysis numbers agreeing with the formula of a nitrobromocinnamic acid. This *paranitrobromocinnamic acid*, when purified by recrystallisation from water, forms very slender needles, having a faintly yellow colour, and somewhat silky lustre. It is sparingly soluble in cold, more readily in hot water, easily in alcohol, ether, light petroleum, and chloroform, sparingly in hot, nearly insoluble in cold carbon bisulphide. Its ethylic ether, obtained by passing hydrochloric acid gas

into its warm alcoholic solution, melts at  $93^{\circ}$ , and agrees in all other respects with that already described.

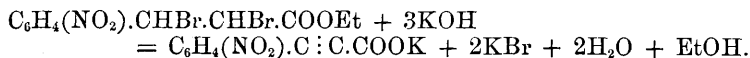
The *barium salt*,  $(\text{C}_6\text{H}_4(\text{NO}_2).\text{C}_2\text{HBr.COO})_2\text{Ba}$ , obtained by dissolving the acid in baryta-water, forms a yellowish crystalline mass. Its aqueous solution boiled or evaporated on a water-bath, is resolved into nitrophenylacetylene, barium bromide, and carbon dioxide :



When the filtrate from the acid melting at  $205^{\circ}$  was shaken with ether, and the residue left after distilling off the ether was dissolved in a small quantity of hot water and allowed to cool, it deposited a substance melting at  $200\text{--}204^{\circ}$ , and therefore essentially identical with the acid above described; but on again treating the filtrate with ether, and repeating the treatment, another paranitrobromocinnamic acid was obtained, melting at  $140\text{--}150^{\circ}$ , and the liquid filtered therefrom and similarly treated yielded a product melting at  $146^{\circ}$ , and therefore the same as the last. This acid dissolves readily in alcohol, ether, and chloroform, sparingly in hot, scarcely at all in cold carbon bisulphide. It is distinguished from the acid melting at  $205^{\circ}$  by greater solubility in cold water. Its ethylic ether is identical with that above described as melting at  $63^{\circ}$  (p. 842). Its barium salt resembles in appearance that of the acid melting at  $205^{\circ}$ , and is likewise resolved by boiling with water into nitrophenylacetylene,  $\text{BaBr}_2$  and  $\text{CO}_2$ .

The preceding facts show that the action of 2 mols.  $\text{KOH}$  in alcoholic solution on 1 mol. ethylic paranitrophenyldibromopropionate, does not take place altogether in the manner indicated by the equation above given (p. 841). One part of the compound ether gives off half its bromine as hydrogen bromide, *without saponification*; another portion is at the same time *saponified*; while a third portion gives off the whole of its bromine, and *is saponified*.

To obtain paranitrophenylpropionic acid from ethylic paranitrophenyldibromopropionate, the author treated 1 mol. of this ether with 3 mols.  $\text{KOH}$  dissolved in alcohol, the reaction taking place as follows :



Paranitrophenylpropionic acid separated from the resulting potassium salt by sulphuric acid, and purified by dissolving it in ether, distilling off the ether, and crystallising the residue from alcohol, remains, on evaporating off the alcohol, as a yellow mass, having a silky lustre, easily soluble in alcohol, soluble also in water, sparingly in chloroform, very sparingly in carbon bisulphide, and quite insoluble in light petroleum. It melts with decomposition at  $181^{\circ}$ , a sublimate of colourless needles collecting in the upper part of the tube. By distillation with steam, it is resolved into paranitrophenylacetylene and  $\text{CO}_2$ .

*Action of Alcoholic Potash on Ethylic Orthonitrophenyldibromopropionate.*—By acting on 1 mol. of this ether in alcoholic solution with 3 mols. alcoholic potash, and treating the product in the manner above described for the para-compound, a brown mass interspersed with

small crystals is obtained; and on drenching this mass with water, exhausting with ether, separating the ethereal extract from the watery solution, and distilling off the ether, a brown crystalline residue is left, which may be purified by distillation with steam. A white flocculent body then passes over with the water, while a small quantity of resinous matter remains in the retort. The body extracted from the distillate by ether is *orthonitrophenylacetylene*. It is very much like the isomeric para-compound; has a similar but more unpleasant odour; yields a red copper-compound and a yellow silver-compound; melts without decomposition at  $80^{\circ}$ ; dissolves readily in alcohol, ether, chloroform, light petroleum, carbon bisulphide, and hot water; less readily in cold water. The hot saturated solution deposits it on cooling, in slender colourless needles.

The clear red aqueous solution, freed from the nitrophenylacetylene by agitation with ether, contains the potassium salt of *orthonitrophenylpropionic acid*,  $C_6H_4(NO_2).C:C.COOK$ , from which the acid itself may be separated by sulphuric acid. This acid, purified by fractional precipitation from solution in ether, and removal of the ether by distillation, remains in the form of a colourless or faintly-reddish mass, having a silky lustre. It melts with decomposition at  $157^{\circ}$  to a brown-red mass, but yields no perceptible sublimate. It is easily soluble in hot water, soluble also in cold water, alcohol, and ether, very slightly in chloroform, nearly insoluble in light petroleum and carbon bisulphide. By distillation with steam, it is resolved into  $CO_2$  and *orthonitrophenylacetylene*, which separates from the distillate in slender needles. Its ethereal solution readily absorbs bromine, forming a compound, which on leaving the ether to evaporate, remains as a clear yellow oil having a peculiar odour. A similar liquid bromide, smelling like rose-oil, is obtained from the para-compound.

*Orthonitrophenylacetylene* is very easily reduced. Its hot aqueous solution mixed with potash-ley, and then with ferrous sulphate, immediately yields a red precipitate of ferric hydroxide; and if the addition of the ferrous sulphate be continued till a black precipitate is formed, the alkaline solution then shaken with ether, and the ether left to evaporate, the reduction-product is obtained as a thick, yellow, non-solidifying oil, having a strong, somewhat fecal, and at the same time sweetish odour, resembling in the dilute state that of the jasmine. This body is *ortho-amidophenylacetylene*,  $C_6H_7N = C_6H_4(NH_2).C:CH$ , its empirical formula being identical with that of indole. Its hydrochloride is a white solid body, turning brown on exposure to light.—*Paranitrophenylacetylene*, treated in like manner with ferrous acetate and potash, yielded nothing but resinous products.

Very interesting results are obtained by the reduction of *orthonitrophenylpropionic acid*. On treating the alkaline solution of this acid with excess of ferrous sulphate, agitating, and filtering, the yellow filtrate becomes covered with shimmering metallic films of indigo-blue. A similar result is obtained with hydrogen sulphide, the indigo, however, then separating as a blue precipitate. *Orthonitrophenylpropionic acid* may also be reduced with tin and hydrochloric acid, the product, however, being not a dye-stuff, but probably the amido-acid of *o*-nitrophenylpropionic acid, or its inner anhydride, a body related to carbo-

styryl in the same manner as orthoamidophenylpropionic acid to orthoamidocinnamic acid, as indicated by the formula

$$\begin{array}{c} \text{C}_6\text{H}_4.\text{NH} \\ | \\ \text{C}:\text{C.CO} \end{array}$$

*Action of Water at High Temperatures on Ethylic Para- and Orthonitrophenyldibromopropionate.*—The para-ether is but little if at all attacked by boiling with water; but when 1 pt. of it is heated with 40 pts. water for three or four days, in a sealed tube at 120–130°, the tube on cooling is found to be filled with slender yellowish-red needles, together with a small quantity of a brown resin; at higher temperatures this resin is formed in larger proportion. The crystalline mass is insoluble in water, whether hot or cold; it dissolves, however, in aqueous sodium carbonate, and on filtering the turbid solution, agitating with ether, which takes up the colouring resin, and finally decomposing the sodium salt with sulphuric acid, a precipitate is obtained, which may be collected and thoroughly washed with hot alcohol. The resulting solution on cooling yields nearly the whole quantity of the product in slender very brilliant needles (m. p. 274°), consisting of paranitrocinnamic acid,  $\text{C}_9\text{H}_7(\text{NO}_2)\text{O}_2$ .

The liquid present in the tube, together with the crystals, was yellow, had a strong acid reaction, and contained a large quantity of hydrobromic acid. On distilling it, the distillate deposited a very small quantity of a colourless body, which reduced silver nitrate at ordinary temperatures. A small quantity of resin remained in the retort.

*Ethylc Orthonitrophenyldibromopropionate* reacts with water nearly in the same manner as the para-compound, being scarcely or not at all attacked at the boiling heat. When heated with water in sealed tubes, it shows a great tendency to resinise, so that it is best not to raise the temperature above 120°. After two or three days' heating, the cooled tube is found to be filled with yellowish capillary crystals, mixed with a moderate quantity of brown resin; no pressure was perceptible on opening. On treating the crystalline mass in the same way as the para-compound, and finally recrystallising from alcohol, an acid was obtained in felted masses of slender needles, melting at 232°, and consisting of orthonitrocinnamic acid. The liquid accompanying the crystals was yellow, had an acid reaction, and contained hydrobromic acid. On distillation, it left a resin and yielded a clear distillate, which reduced ammoniacal silver solution, but contained no more than traces of a body extractable by ether. The quantity of orthonitrocinnamic acid obtained was about two-thirds of the theoretical.

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The preceding results show that the tendency of cinnamic acid to unite with negative radicles, and pass into a saturated compound, is greatly weakened by the entrance of the nitro-group into its benzene-nucleus. Cinnamic acid itself readily takes up  $\text{Br}_2$  or  $\text{HBr}$ , but the combination of the nitrocinnamic acids with bromine takes place slowly and with difficulty, and similarly with the hydrogen haloids. By neutralisation, *i.e.*, conversion into alkyl salts, on the other hand, this influence of the nitro-group is weakened, inasmuch as the nitrocinnamic ethers combine readily with bromine. In like manner,

Beilstein and Kupfer have shown (*Ber.*, **12**, 1688) that paranitrocinnamic acid in alkaline solution easily takes up hypochlorous acid. Very remarkable, also, is the fact that the two bromine-atoms in the nitrophenyldipropionic ethers are easily removed by heating with water in sealed tubes, the ether being at the same time saponified, and nitrocinnamic acid reproduced. Moreover, the *substitution-products* resulting from the replacement of hydrogen in the side-chain of nitrocinnamic acid by negative radicles hold these radicles less firmly than the corresponding derivatives of cinnamic acid, as shown by the easy conversion of paranitrobromocinnamic acid and its salts into paranitrophenylpropionic acid. In the nitrophenylpropionic acid even the retention of the carboxyl-group is very much weakened by the influence of the nitro-group, these acids giving up  $\text{CO}_2$  even on boiling with water, whereas phenylpropionic acid, as shown by Glaser, undergoes this decomposition only at  $120^\circ$  in sealed tubes. H. W.

**Derivatives of Paranitrocinnamic Acid.** By V. R. DREWSSEN (*Annalen*, **212**, 150—165).—This paper travels partly over the same ground as the preceding. The *p*-nitrocinnamic acid, prepared by the method there described, was found to melt at  $288^\circ$  (? corrected; Müller, whose temperatures are all uncorrected, gives it at  $276^\circ$ , (see p. 841).

*Dibromide of Paranitrocinnamic acid* or *Paranitrophenyl-dibromopropionic acid*,  $\text{C}_6\text{H}_4\text{NO}_2\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{COOH}$ , prepared by exposing finely pulverised *p*-nitrocinnamic acid to the action of gaseous or liquid bromine, crystallises from glacial acetic acid in well-defined rhombic prisms with brachydiagonal faces; they become opaque on exposure to the air, and melt at  $217\text{--}218^\circ$ . The acid is extremely soluble in water; but is decomposed by prolonged boiling, giving off an odour like that of acetylene. It dissolves readily in alcohol and ether, with moderate facility in hot glacial acetic acid, sparingly in benzene, and is nearly insoluble in light petroleum. All its salts are decomposed by boiling with water. The *barium salt* crystallises in monoclinic prisms moderately soluble in cold water. The *sodium salt* dissolves easily in water, with difficulty in alkalis, and is precipitated from the aqueous solution by excess of soda-ley in glimmering laminæ. The solid sodium salt dissolves in excess of soda-ley, and, on addition of an acid, the solution deposits white flocks, consisting of a mixture of paranitrophenylpropionic acid (m. p.  $198^\circ$ ) and paranitrocinnamic acid. The dibromide treated with alcoholic potash, is entirely converted into paranitrophenylpropionic acid.

*Dibromide of Ethylic Paranitrocinnamate* or *Ethylic Paranitrophenyldibromopropionate*,  $\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{COOEt}$ , prepared by direct combination, was found by the author to crystallise in monoclinic prisms melting between  $113^\circ$  and  $116^\circ$  (according to Müller, at  $110\text{--}111^\circ$ ).

*Paranitrophenylpropionic acid*,  $\text{C}_6\text{H}_5\text{NO}_3$ , prepared as described in the preceding paper by the action of alcoholic potash on ethylic *p*-nitrophenyldibromopropionate, melts, according to Drewsen, at  $198^\circ$  (according to Müller at  $181^\circ$ ). Its *silver salt* is an amorphous, slightly yellowish powder, which dissolves sparingly in water, is slowly decom-

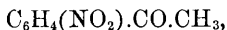
posed by light, detonates strongly, when heated, and is decomposed with incandescence by strong nitric acid. The *calcium salt* crystallises from water in slender needles. The *barium salt* forms needles slightly soluble in water. Both these salts detonate when heated, and are decomposed by boiling with water. The *ethylic ether*, prepared by passing HCl gas into the alcoholic solution of the acid, crystallises in long flat needles melting at  $126^{\circ}$ .

*Dibromide of Paranitrophenylpropionic acid* or *Paranitrodibromocinnamic acid*,  $C_6H_4(NO_2).CBr : CBr.COOH$ , prepared by leaving *p*-nitrophenylpropionic acid in an atmosphere of bromine for 24 hours, then expelling the excess of bromine, and crystallising the resulting yellow substance from a small quantity of hot glacial acetic acid, forms hard brittle crystals which begin to soften at  $176^{\circ}$ , and melt at  $179-180^{\circ}$ . It dissolves readily in alcohol, ether, and hot glacial acetic acid, less easily in benzene, and is nearly insoluble in light petroleum.

The *ethylic ether*,  $C_6H_4(NO_2)_2.C_2Br_2.COOEt$ , obtained in like manner from ethylic *p*-nitrodibromocinnamate, forms crystals melting at  $85-86^{\circ}$ , easily soluble in benzene, chloroform, and glacial acetic acid, sparingly in light petroleum.

*Paranitrophenylacetylene*,  $C_6H_4(NO_2)_2.C : CH$ , obtained by heating *p*-nitrodibromocinnamic acid in sealed tubes at  $140^{\circ}$ , forms crystals melting at  $152^{\circ}$ , becoming brownish on exposure to light, easily soluble in hot alcohol, ether, chloroform, benzene, and glacial acetic acid, sparingly in light petroleum. It is likewise dissolved in considerable quantity by hot water, and separates therefrom on cooling in slender needles. Its odour is very much like that of cinnamon.

*Paranitroacetophenone* or *Methylparanitrophenyl Ketone*,



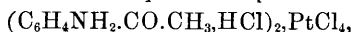
is formed, with evolution of carbon dioxide, on heating paranitrophenylpropionic acid at  $100^{\circ}$  with sulphuric acid—best with a mixture of 3 pts.  $SO_4H_2$  to 1 pt. water. On adding water to the resulting liquid, a brown mass separates out, which may be freed from undecomposed acid by washing with sodium carbonate, then dried, and treated with carbon bisulphide, the yellow solution on evaporation depositing yellow crystals of the ketone, which may be purified by crystallisation from hot water, and then forms slightly yellowish prisms melting at  $80-81^{\circ}$ . This body is not dissolved either by acids or by alkalis; it gives no precipitate with ammoniacal cuprous chloride, and is not altered by boiling with acetic anhydride or by treatment with acetic chloride; but when treated with phosphorus pentachloride it is decomposed in the manner shown by the equation  $C_6H_4(NO_2).CO.CH_3 + PCl_5 = POCl_3 + C_6H_4(NO_2).CCl_2.CH_3$ , yielding *paranitrodichlorethylbenzene*, which is immediately resolved into HCl and *paranitrochlorocinnamene*,  $C_6H_4(NO_2).CCl : CH_2$ . This last body is sparingly soluble in water, but dissolves readily in most other solvents, crystallises from light petroleum in concentric groups of light yellow needles, and may be completely purified by once recrystallising it from hot alcohol; it then melts at  $63-64^{\circ}$ .

*Paramidacetophenone*,  $C_6H_4(NH_2).CO.CH_3$  is formed by heating the nitro-ketone with tin and hydrochloric acid, whereupon a violent



action takes place, the whole dissolves, and the solution on cooling deposits the stannochloride of paramidacetophenone; and on diluting the solution with water, passing hydrogen sulphide through it till all the tin is precipitated, and evaporating the filtered liquid, the hydrochloride of the paramido-ketone crystallises out in long slender needles. The solution of this salt, treated with soda-ley, deposits the base in shining laminae.

Paramidacetophenone is eminently crystallisable; it dissolves easily in boiling water, and separates on cooling in fan-shaped groups of long crystals traversing the entire liquid. Its *platinochloride*,



crystallises in small yellow anhydrous needles.

On passing nitrous gas through cooled alcohol in which paramidacetophenone sulphate was suspended, decomposing the resulting diazo-compound with boiling alcohol, then driving off the alcohol, and distilling the residue with steam, a colourless non-azotised oil passed over, possessing in a high degree the characteristic odour of acetophenone, but the quantity obtained was too small for complete examination.

H. W.

**Acids obtained from Xylene and Phthalic Anhydride.** By F. MEYER (*Ber.*, 15, 636—638).—The author has studied the acids formed by the action of xylene and its homologues on phthalic anhydride in presence of aluminium chloride. As regards their nomenclature, the grouping,  $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}$ , derived from phthalic acid is denominated “phthaloyl.”

*Orthoxylenephthalic acid*,  $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$  [Me : Me = 1 : 2], from orthoxylene and phthalic anhydride, crystallises in microscopic prisms (m. p.  $161^\circ$ ); when fused with potash, it is decomposed into benzoic and paraxylic (m. p.  $161^\circ$ , b. p.  $280^\circ$ ) acids.

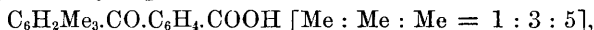
*Metaxylenephthalic acid*,  $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$  [Me : Me = 1 : 3], from metaxylene and phthalic anhydride crystallises in needles; when fused with potash, it is decomposed into benzoic and ordinary xylic (m. p.  $126^\circ$ ) acids.

*Paraxylenephthalic acid*,  $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$  [Me : Me = 1 : 4], from paraxylene and phthalic anhydride, was obtained only in the form of a glassy mass, and not in crystals; it is decomposed into benzoic and isoxylic acid when fused with potash.

*Pseudocumenephthalic acid*, formed by an analogous method, melts at  $146\cdot5^\circ$ .

V. H. V.

**Mesitylenephthalic Acid.** By J. GRESLY and F. MEYER (*Ber.*, 15, 639).—*Mesitylenephthalic acid*,

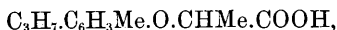


from phthalic anhydride and mesitylene, crystallises from acetic acid in rhombohedra (m. p.  $212^\circ$ ); it is very sparingly soluble in water and in dilute alcohol.

V. H. V.

**Thymolactic Acid.** By S. SCICCHILONE (*Gazzetta*, 12, 48—51).—A mixture of synthetic thymol with chloropropionic acid (prepared from lactic chloride) is heated for a few minutes at  $100^\circ$ , and a con-

centrated solution of potash is then gradually poured in; the mixture, at first homogeneous, soon separates into two layers. It is heated for two hours in a water-bath, diluted with water, acidified with hydrochloric acid, and then neutralised with ammonium carbonate; in this way the unaltered thymol is set free, and may be removed by repeated agitation with ether. On adding hydrochloric acid in excess to the solution of ammonium thymolactate, the thymolactic acid,



is precipitated as a light oil, which solidifies in a short time to a mass of transparent needles. The author was not successful in his attempts to purify the acid by crystallisation from the ordinary solvents, but obtained it perfectly pure by precipitation from the potassium salt. It crystallises in prisms (m. p.  $74^\circ$ ), exceedingly soluble in alcohol, ether, and chloroform.

The thymolactic acid, prepared from natural thymol in a precisely similar manner, melts at  $48^\circ$ . The barium salt is left on evaporating its solution as a white, very soluble powder, which could not be obtained in the crystalline state. The silver salt is thrown down as a white non-crystalline powder on adding silver nitrate to a solution of the acid in dilute ammonia.

C. E. G.

**Behaviour of Orthonitrophenoxyacetic Acid with Reducing Agents.** By A. THATE (*J. pr. Chem.*, **25**, 265—267).—By boiling the anhydride,  $\text{C}_6\text{H}_7\text{NO}_2$  (Fritzsche, this Journal, **38**, 320), with hydrochloric acid for 48 hours, the author obtained a homogeneous body,  $\text{C}_6\text{H}_6\text{ClNO}_2$  (m. p.  $197^\circ$ ), bearing great resemblance to the anhydride (which melts at  $143$ — $144^\circ$ ). The anhydride yields crystalline bodies when it is treated with nitrous acid, bromine, and acetic anhydride. If orthonitrophenoxyacetic acid is reduced in alkaline solutions with sodium-amalgam, *azo-orthophenoxyacetic acid*,  $\text{COOH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{COOH}$ , is obtained. It crystallises in small yellow-red needles, soluble in water, alcohol, ether, benzene, and alkalis, with a yellow, and in hydrochloric acid with a red colour. It has a slightly acid reaction. It melts at  $151$ — $152^\circ$  to a wine-red fluid, and, on further heating, decomposes, giving off a yellow vapour; it finally burns, and leaves behind a voluminous charcoal. It forms characteristic salts; the silver salt is feebly explosive.

D. A. L.

**Solubility of Aluminium Gallate in Water.** By A. LIDOFF (*Jour. Russ. Chem. Soc.*, 1882, 195—196).—A sample of tannin (extract of chestnut) analysed by the author was found to contain 20.33 per cent. of tannic acid and 12.42 of gallic acid. The latter was converted first into the sodium salt, and afterwards into the aluminium salt, and its solubility in 100 parts of water was found to be as follows:—

	At $20^\circ$	$40^\circ$	$60^\circ$	$80^\circ$	$100^\circ$
Pts. of salt	2.02	1.43	0.99	0.87	0.84

B. B.

**Electrolysis of various Solutions, Acid, Neutral, and Alkaline, with Graphite Electrodes.** By A. BARTOLI and G. PAPASOGLI (*Gazzetta*, 1882, 113—117).—The graphite used in these experiments was good Ceylon graphite, freed from every trace of hydrogen by prolonged heating at the melting point of iron, sometimes in a current of chlorine.

*Electrolysis of Alkaline Solutions.*—In solutions of potassium or sodium hydroxide electrolysed by the current of four large Bunsen's cells, sometimes for a few days only, sometimes for two months, a considerable quantity of gas was evolved at the negative, and only a small quantity at the positive electrode, the graphite at the same time losing but little in weight. At the end of the experiment there was found at the bottom of the voltameter a small deposit of graphite. The supernatant liquid was limpid and colourless, effervesced slightly with acetic acid; and the acidulated solution gave with calcium chloride a copious precipitate of calcium mellate,  $C_{12}Ca_3O_{12}$ . The filtrate, after neutralisation with potash, gave a precipitate with barium nitrate; on converting this into sodium salt, then into lead salt, and decomposing the latter with hydrogen sulphide, an acid liquid was obtained, which, when neutralised with ammonia, yielded crystals of ammonium pyromellate together with non-crystalline hydromellate.

*Acid and Neutral Solutions.*—In solutions of mineral acids and of neutral salts, e.g., the nitrates and sulphates of potassium and sodium, the graphite forming the positive electrode is quickly disintegrated, and at the bottom of the voltameter there is formed a thick deposit of very minute graphite scales mixed with another substance, less shining and altogether of different aspect. On washing this deposit (obtained in the electrolysis of sulphuric acid) till it no longer contained a trace of acid, drying at  $100^\circ$ , then passing it through a sieve to separate the graphite scales, and finally separating the lighter particles of graphite by washing and levigation, a very fine dark-coloured powder was obtained, insoluble in all solvents either hot or cold, swelling up strongly at  $300^\circ$ , and changing to a black shining powder which does not make a mark on paper. This black powder contains carbon, hydrogen, and oxygen, and gives by analysis numbers agreeing nearly with the formula of graphitic acid,  $C_{11}H_4O_6$ . It contains also small quantities of graphite not removed by levigation, and of another substance which by oxidation with alkaline hypochlorites is converted into mellic acid.

H. W.

**Mellogen, a New Compound obtained by Electrolysis.** By A. BARTOLI and G. PAPASOGLI (*Gazzetta*, 1882, 117—124).—In previous publications (*Accad. dei Lincei*, 8, 89, Anno 1879—80; *Cimento*, 8, 278; 10, 204, and this vol., p. 406), the authors have stated that when water is decomposed by a powerful electric current, with a positive electrode of gas-coke purified by the action of chlorine at a very high temperature, there is obtained, besides mellic and other benzene-carboxylic acids, a new substance, which they call mellogen, from its property of yielding mellic acid by oxidation. Having now obtained this substance in larger quantity, they have been able to determine its composition and study its properties more easily.

About a kilogram of purified gas-coke having been disintegrated, as already described (p. 850) by the electrolysis of water with a very powerful battery (1200 Daniell), the black acid liquid in the voltmeter was filtered through asbestos, and evaporated nearly to dryness on a water-bath, whereupon the mellogen was deposited in the form of a very fine black powder, which was collected on a filter and washed with water. A larger quantity of mellogen may, however, be obtained from the black deposit at the bottom of the voltmeter, by washing this deposit with distilled water by decantation in tall glass cylinders till the wash-waters become nearly colourless, and acidifying the united washings with hydrochloric acid, whereupon the mellogen is precipitated in dark flocks, which unite at the bottom of the vessel, and may be collected on a filter and washed with distilled water.

Pure mellogen, dried under a bell-jar with sulphuric acid, is a black solid shining substance, having a conchoidal fracture and easily pulverised. It is insoluble in methyl, ethyl, and amyl alcohols, also in ether, benzene, chloroform, carbon bisulphide, and oil of turpentine; soluble in water, which it colours black; also in ammonia, caustic potash and soda, and in sodium carbonate, forming liquids of inky blackness. It dissolves also with dark colour in strong sulphuric acid, but the addition of a small quantity of water renders the liquid limpid and throws down a black precipitate. Mellogen dried over sulphuric acid decrepitates on addition of water, the water suddenly becoming black. Mellogen does not melt when heated; burns with difficulty, and without tumefaction. It is not crystalline; neither do its solutions in ammonia or the fixed alkalis yield any crystals. It fixes itself tenaciously on vegetable fibres. Its aqueous solution, which is difficult to filter, dyes the paper a fine shining black; and the immersed parts of the filter, after drying, adhere so strongly to one another and to the funnel, that they cannot be separated without tearing.

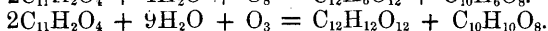
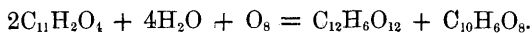
The aqueous solution of mellogen is neutral and black as ink, and remains so after repeated filtration and long keeping, even for a year. It is completely precipitated after a moderate interval—leaving the supernatant liquid perfectly limpid—by dilute solutions of hydrochloric, hydriodic, sulphuric, nitric, phosphoric, chromic, oxalic, and formic acids (with the last, however, the supernatant liquor remains slightly yellowish); further by solutions of bromine, chlorine, and iodine; of sulphate, chromate, dichromate, nitrate, thiocyanate, ferrocyanide, ferricyanide, acid carbonate, acid sulphite, and sulphide of potassium and sodium; by calcium and barium hydroxides; by all the mineral salts of magnesium, zinc, cadmium, iron (ferrous or ferric), manganese, copper, lead, silver, &c. On the other hand, the aqueous solution of mellogen retains its inky blackness for many days after the addition of aqueous solutions of acetic, propionic, lactic, tartaric, tannic, picric, mellic, hydromellic, pyromellic, citric, caproic, butyric, valeric, carbonic acid, &c.; also after addition of solutions of methyl or ethyl alcohol, glycerol, saccharose, lactose, dextrin, &c., or of sodium phosphate or ammonium oxalate.

The black precipitates obtained with hydrochloric, nitric, and sulphuric acid, or with sodium chloride or sulphate, ammonium sulphate, potassium bromide, silver nitrate, &c., when collected on a filter and

washed with water, redissolve in the water after a certain number of washings, forming inky liquids capable of reprecipitation by the same salts; but the precipitates obtained with barium hydroxide or chloride, copper sulphate, and lead acetate, remain undissolved even after washing for several weeks.

Pure dry mellogen dissolves in nitric acid of sp. gr. 1.3, with evolution of nitrous vapours; and on evaporating to dryness over the water-bath and redissolving in water, a solution is obtained, red by transmitted light, neutral to test-papers, and incompletely precipitated by solutions of hydrochloric or sulphuric acid, by chloride, bromide, or iodide of sodium or potassium, or by chloride of calcium, barium, or zinc.

The most remarkable property of mellogen is that of being converted into mellic acid,  $C_{12}H_6O_{12}$ , and some of its derived acids, viz., pyromellic,  $C_{10}H_6O_8$ ; hydromellic,  $C_{12}H_{12}O_{12}$ ; and hydropyromellic acid,  $C_{10}H_{10}O_8$ , by the action of oxidising agents, and even on exposure to the air, but most readily by the action of soluble hypochlorites. The formation of these compounds is explained by the following equations, mellogen, as shown by its analysis and that of several of its salts, having the composition  $C_{11}H_2O_4$ .



Mellogen, in many of its properties, differs considerably from Brodie's graphitic acid, as the following comparison will show:—

*Mellogen*,  $C_{11}H_2O_4$  (at  $140^\circ$ ).

1. Entirely transformed by hypochlorites into mellic and pyromellic acids.

2. Soluble in water, alkalis, and strong sulphuric acid; dissolves in fuming nitric acid, with evolution of nitrous vapours.

3. Does not swell up when heated.

*Graphitic acid*,  $C_{11}H_4O_5$  (at  $100^\circ$ ).

1. Gives no product of transformation with hypochlorites.

2. Insoluble in all liquids, acid, alkaline, or neutral; not attacked by fuming nitric acid.

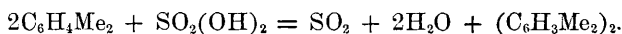
3. Swells up when heated, and is converted into pyrographitic acid.  
H. W.

**Electrolysis of Phosphoric Acid Solutions with Electrodes of Gas-coke and Graphite.** By A. BARTOLI and G. PAPASOGLI (*Gazzetta*, 1882, 125—128).—1. With gas-coke electrodes, there is formed a black substance insoluble in the electrolyte but soluble in alkalis; it contains phosphorus, and when heated with sodium hypochlorite, yields phosphoric acid, together with mellic, pyromellic, and other hydrobenzenecarboxylic acids. The authors propose to designate this substance as phosphomellogen.

2. With electrodes of graphite, there is obtained, instead of graphitic acid, a product which contains phosphorus, and does not tumefy when heated, probably a phosphorised compound analogous in composition to graphitic acid.  
H. W.

**Isohydrobenzoïn Carbonate.** By M. WALLACH (*J. pr. Chem.* [2], 25, 262—265).—By the action of sodium-amalgam on a mixture of equivalent quantities of benzaldehyde and ethyl chlorocarbonate, the author obtained a crystalline substance (m. p.  $110^{\circ}$ ) which, when boiled with alcoholic potash, decomposes, yielding potassium carbonate, a small quantity of an oil, and crystals of isohydrobenzoïn (m. p.  $119^{\circ}$ ). The crystalline substance is therefore isohydrobenzoïn carbonate. It is insoluble in cold water, alcohol, ether, and carbon bisulphide; slightly soluble in boiling water, easily in warm alcohol and ether, and in cold benzene. The crystals are monoclinic leaflets. It can be partially sublimed with decomposition. D. A. L.

**Dixylene and its Products of Oxidation.** By V. OLIVERI (*Gazzetta*, 1882, 158—161).—Jacobsen showed, in 1877, that commercial xylene is a mixture of the three isomeric xylenes, and that on treating it at a moderate heat with ordinary sulphuric acid, the paraxylene remains unattacked, while the ortho- and meta-xylene dissolve; at the same time there is formed a paraffin boiling at  $150^{\circ}$  (this *Journal*, 32, 600). Oliveri now finds that, in addition to this reaction, a more complex one takes place, consisting in the formation of a dixylene ( $C_{16}H_{18} = 2C_8H_{10} - H_2$ ), the eliminated hydrogen at the same time reducing the sulphuric acid to sulphurous oxide:



Commercial xylene boiling at  $138$ — $140^{\circ}$  was heated in a water-bath with  $1\frac{1}{2}$  vols. sulphuric acid of ordinary strength, and the product, after cooling, was mixed with a large quantity of water to separate the undissolved oil, which was distilled in a current of steam. Paraxylene then passed over, and the portion which remained in the flask, when separated from the water by a tap-funnel, washed repeatedly with distilled water, then dried over calcium chloride, and distilled, passed over for the most part at  $285$ — $300^{\circ}$ , and this distillate, after being left for a day in contact with sodium and again distilled and rectified, passed over entirely at  $293$ — $297^{\circ}$ .

The product thus obtained is dixylene: it is a colourless, strongly refractive, fluorescent liquid, lighter than water, and smells like balsam of copaiba. It appears to be identical with the dixylene (b. p.  $290$ — $295^{\circ}$ ) which Fittig, Ahrens and Mattheides obtained by the action of sodium on bromometaxylylene dissolved in toluene (*Bull. Soc. Chim.*, 1868, 464), whence it would follow that the condensing action of sulphuric acid on a mixture of xylenes is exerted solely on the metaxylylene; but the experiments hitherto made to decide this point, and determine the orientation of the side-chains in the dixylene obtained as above, have not yielded satisfactory results. H. W.

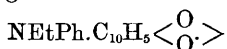
**Compounds of Naphthoquinone with Toluidine and Ethylaniline.** By L. ELSBACH (*Ber.* 15, 685—694).—Liebermann has established that the conversion of  $\beta$ -naphthoquinoneanilide into the corresponding  $\alpha$ -compound is the result of the decomposition of the anilide into hydroxynaphthoquinone and the free base, which subsequently recombine to form  $\alpha$ -naphthoquinoneanilide. To the  $\beta$ -com-

pound Liebermann assigns the constitution  $\beta \text{ OH.C}_{10}\text{H}_5 < \begin{smallmatrix} \text{NPh} \\ \text{O} \end{smallmatrix} > \begin{smallmatrix} \alpha \\ \alpha' \end{smallmatrix}$ , based more especially on its solubility in alkalis, but to the  $\alpha$ -compound the constitution  $\beta \text{ NPh.C}_{10}\text{H}_5 < \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix} > \begin{smallmatrix} \alpha \\ \alpha' \end{smallmatrix}$ . The author has extended Liebermann's researches and examined the corresponding toluidine derivatives.

$\beta$ -Naphthoquinone *p*-toluidide, obtained from  $\beta$ -naphthoquinone and *p*-toluidine, crystallises in reddish needles (m. p. 246°), sparingly soluble in ether and alcohol; like the corresponding anilide, it is soluble in dilute alkalis, and is reprecipitated by acid.  $\alpha$ -Naphthoquinone-*p*-toluidide, prepared by a method similar to the  $\beta$ -compound, melts at 202° and resembles the  $\beta$ -compound in most of its properties except that it is insoluble in dilute alkalis. On heating  $\beta$ -naphthoquinone-*p*-toluidide with acetic acid in sealed tubes at 150°, it is converted into the  $\alpha$ -compound; when heated with hydrochloric acid, it yields hydroxynaphthoquinone and toluidine, which recombine to form  $\alpha$ -naphthoquinone-*p*-toluidide.

$\beta$ -Naphthoquinone-*o*-toluidide, from  $\beta$ -naphthoquinone and ortho-toluidine, crystallises in red needles (m. p. 240°), soluble in dilute alkalis with formation of a yellow solution. On heating with dilute hydrochloric acid, it is decomposed into hydroxynaphthoquinone and orthotoluidine, which will recombine to form  $\alpha$ -naphthoquinone-*o*-toluidide, crystallising in delicate red needles (m. p. 140°).

The author has further examined the product of the action of a secondary amine, as ethylaniline, on  $\beta$ -naphthoquinone, which, according to Liebermann's view should possess a constitutional formula,  $\alpha \text{ NPhEt.C}_{10}\text{H}_5 < \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix} > \begin{smallmatrix} \beta \\ \alpha \end{smallmatrix}$ , and would differ from  $\beta$ -naphthoquinone-anilide by being insoluble in alkalis. By the action of ethylaniline on  $\beta$ -naphthoquinone, a  $\beta$ -naphthoquinonethylanilide was obtained, crystallising in dark-red needles (m. p. 165°), which was insoluble in alkalis, but was decomposed by acids into hydroxynaphthoquinone and the free base. This compound is isomeric with the ethyl ether of  $\beta$ -naphthoquinoneanilide obtained by Zincke; the latter possessing the constitution  $\text{OEt.C}_{10}\text{H}_5 < \begin{smallmatrix} \text{NPh} \\ \text{O} \end{smallmatrix} >$ , the former the constitution



V. H. V.

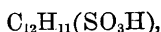
**Dimethylnaphthalene.** By G. GIOVANNONZI (*Gazzetta*, 1882, 147—151).—This compound was prepared by heating in a reflux apparatus 100 grams of dibromonaphthalene (m. p. 81°), dissolved in toluene, with a large excess (350 g.) of methyl iodide and 40 g. sodium cut up into small pieces. The reaction took place easily at the boiling point of the methyl iodide, and on its completion the liquid was distilled at 150° to expel the excess of methyl iodide and the toluene. The residue treated with ether yielded a deep red fluorescent liquid, from which, on fractional distillation, a portion was obtained passing over at 260—270°; and this, when redistilled under reduced pressure, yielded about 20 g. of liquid boiling at 135—140°. This liquid, how-

ever, contained unaltered dibromonaphthalene, the greater part of which was removed by prolonged boiling with sodium; also naphthalene regenerated in the reaction, from which it was completely freed by keeping it for some time at  $100^{\circ}$  in an exhausted vessel. The last portions of dibromonaphthalene were separated by treating the product with picric acid, which precipitated the dimethylnaphthalene as picrate, leaving the dibromonaphthalene in solution. The dimethylnaphthalene was then separated from the picrate by ammonia.

Dimethylnaphthalene,  $C_{12}H_{12} = C_{10}H_6(CH_3)_2$ , is a colourless oily strongly refracting liquid, having a faint odour of naphthalene; it remains liquid at  $-18^{\circ}$ , and boils with partial alteration above  $265^{\circ}$ . Sp. gr. = 1.0176 at  $20^{\circ}$  (water at  $20^{\circ} = 1$ ). Vapour-density: exp. = 5.48; calc. = 5.40. The *picrate* crystallises in fine orange-coloured needles, moderately soluble in hot alcohol, very soluble in ether, melting at  $139^{\circ}$ .

Dimethylnaphthalene, treated with excess of *bromine* at a low temperature, yields a white crystalline product consisting of two substances differing from one another by their solubility in ether. They have not been obtained in sufficient quantity for complete examination, but the less soluble (m. p.  $184^{\circ}$ ) appears to be an addition-product,  $C_{12}H_{12}Br_6$ , and the more soluble, which melts at  $145-147^{\circ}$ , a tribromo-derivative,  $C_{12}H_9Br_3$ .

Dimethylnaphthalene, heated at  $120^{\circ}$  for five or six hours with twice its weight of strong sulphuric acid, yields an acid liquid, from which, by conversion into lead salt, decomposition by hydrogen sulphide, and evaporation, *dimethylnaphthalenesulphonic acid*,



is obtained in white deliquescent crystalline scales. The potassium salt of this acid crystallises in dazzling white nacreous hygroscopic scales having the composition  $C_{12}H_{11}SO_3K + H_2O$ . When fused with potash, it gave some indications of the formation of a phenolic body, but the product consisted mainly of resinous substances impossible to purify.

H. W.

**Reduction in the Anthraquinone Series.** By C. LIEBERMANN (*Annalen*, 212, 1—121).—This paper gives a detailed and systematic account of a series of researches by the author and his pupils on the reduction-products of anthraquinone, separate portions of which have been already published in the *Berlin Berichte* (1876—1881), and abstracts thereof in this Journal (1877—1882).

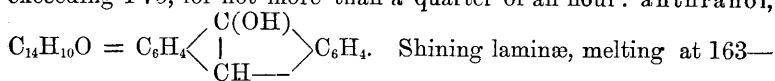
The following is a summary of the whole, together with descriptions of compounds not previously noticed:—

#### PART I.—THE REDUCTION OF ANTHRAQUINONE AND ITS DERIVATIVES.

—(1.) *Reduction of Anthraquinone with Hydriodic Acid and Phosphorus* (Liebermann and Topf, *Ber.*, 9, 1201; *Chem. Soc. J.*, 1877, 1, 86).—The products of this reduction are:  $\alpha$ . In sealed tubes, anthracene.  $\beta$ . In open vessels: (a.) With acid of sp. gr. 1.8, the heating being continued for an hour: anthracene dihydride,  $C_{14}H_{12}$ , crystallising in large laminæ melting at  $107-108^{\circ}$ . (b.) With acid of sp. gr. not



exceeding 1.75, for not more than a quarter of an hour: anthranol,



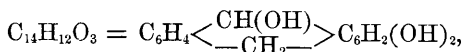
170°. Dissolves in alkalis with yellow colour; in alcohol with bluish fluorescence. Oxidised by chromic acid in glacial acetic acid solution to anthraquinone; reduced by zinc-dust to anthracene.

*Acetyl-anthranol*,  $\text{C}_{14}\text{H}_9\text{AcO}$ , formed by heating anthranol in a sealed tube at 160—170° with acetic anhydride, crystallises from alcohol in white needles melting at 126—131°.

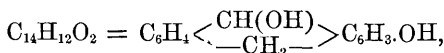
(2.) *Reduction of Quinizarin*.—This compound,



is reduced:  $\alpha$ . By heating for a short time with hydriodic acid of sp. gr. 1.7 and a small quantity of red phosphorus, or with hydrochloric acid and stannous chloride, to hydroquinizarin,  $\text{C}_{14}\text{H}_{10}\text{O}_4 = \text{C}_6\text{H}_4 : \text{C}_2(\text{OH})_2 : \text{C}_6\text{H}_2(\text{OH})_2$ , which crystallises from alcohol in laminæ or needles having a golden lustre.  $\beta$ . By somewhat longer heating, to hydroquinizarol,



crystallising from alcohol in reddish-yellow needles.  $\gamma$ . By heating for an hour with acid of sp. gr. 1.8 to 1.9 and excess of red phosphorus, to hydroxy-hydranthranol,



which, when purified by conversion into potassium salt, separated therefrom by an acid, and crystallised from alcohol, forms yellowish-white rhombic plates melting at 99°. Its *acetyl-derivative* forms pale-yellow warty crystals melting at 136—138°. It reacts easily with ethylamine, forming the compound  $\text{C}_{14}\text{H}_{10}(\text{OH}).\text{NH}\text{Et}$ , crystallising in yellow needles which melt at 162°.

*Oxidation of Hydroxy-hydranthranol*.—When this compound (1 g.), dissolved in 25 g. glacial acetic acid mixed with 5 g. of 20 per cent. sulphuric acid, is boiled for an hour or two with 2 g. of a mixture of manganese dioxide and a small quantity of hausmannite, it is converted, with change of colour from yellow to dark orange, into *erythro-hydroxyanthraquinone*, according to the equation  $\text{C}_{14}\text{H}_{12}\text{O}_2 + \text{O}_3 = 2\text{H}_2\text{O} + \text{C}_{14}\text{H}_8\text{O}_3$ . The quantity of manganese dioxide decomposed is, however, much below that which is indicated by this equation, so that the oxidation must be in great part effected by the oxygen of the air; nevertheless it does not take place without the aid of the manganese oxide. The oxidation-product is precipitated from the filtrate by water in orange-coloured flocks, and purified by crystallisation from alcohol, from which it separates in needles to be further purified by sublimation. It then melts at 190—191°, in which character, as well as in its spectroscopic relations, it agrees with the erythro-hydroxyanthraquinone which von Pechmann has lately obtained from the bromanthra-

quinone prepared from bromobenzoylbenzoic acid (*Ber.*, **12**, 2127; also *Abstr.*, 1880, 323).

The formation of this body, which is known to have the formula  $C_6H_4 : C_2O_2 : C_6H_3.OH$ , from hydroxy-hydranthranol, shows that the latter must be represented by the formula above assigned to it.

Anthracene-derivatives containing the middle group  $\langle \begin{smallmatrix} CH(OH) \\ -CH_2- \end{smallmatrix} \rangle$  are best designated as hydranthranols, in accordance with the name

anthranol applied to those which contain the group  $\langle \begin{smallmatrix} CH \\ | \\ C(OH) \end{smallmatrix} \rangle$ , having

2 at. hydrogen less. The typical member of the hydranthranol group is *dihydranthranol*,  $C_{14}H_{12}O = C_6H_4 \langle \begin{smallmatrix} CH(OH) \\ -CH_2- \end{smallmatrix} \rangle C_6H_4$ , lately obtained by v. Perger (*J. pr. Chem.*, **23**, 17) by reduction of anthraquinone with zinc-dust and ammonia. This compound and its alkyl-derivatives are distinguished by the property of easily giving up 1 mol. water, and yielding hydrocarbons. It is remarkable, however, that this property is not exhibited by hydroxy-hydranthranol.

The formation of erythrohydroxyanthraquinone from quinizarin leads to certain conclusions respecting the orientation of the hydroxyl-groups in the hydroxyanthraquinones. For quinizarin, the structure is determined by the para-position of the hydroxyls in quinol: hence

the formula of erythrohydroxyanthraquinone is  $C_6H_4 \langle \begin{smallmatrix} CO- \\ CO- \end{smallmatrix} \begin{array}{c} OH \\ \diagup \quad \diagdown \\ H \quad H \\ \diagdown \quad \diagup \\ H \end{array} \rangle$ ,

whence may be deduced the position of the hydroxyls in alizarin, &c. (see Fraude, *Ber.*, **12**, 1597; *C. J.*, 1879, *Abstr.*, 636).

(3.) *Reduction of Hydroxyanthraquinone* (Liebermann and Simon, *Ber.*, **14**, 1264; also *Abstr.*, 1881, 123).—This compound (the ordinary yellow modification) was prepared by heating sodium anthraquinonemonosulphonate with 5 pts. soda-ley of 20 per cent. for three or four hours at 155–165°, precipitating at the boiling heat with hydrochloric acid, decomposing the precipitate of hydroxyanthraquinone and a small quantity of alizarin with boiling baryta-water, precipitating the filtered solution of barium hydroxyanthraquinone with hydrochloric acid, and crystallising the precipitate from boiling alcohol. The compound is thus obtained in golden-yellow laminæ melting at 302°.

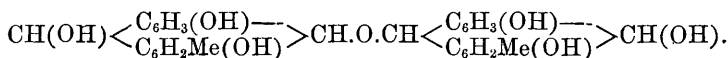
Hydroxyanthraquinone treated with strongly fuming hydriodic acid and about 5 pts. red phosphorus, yields a mixture of anthracene hexhydride,  $C_{14}H_{12}$ , and hydroxyanthracene or anthrol,  $C_{14}H_{10}O$ . After separation of hydriodic acid by washing with water, and the excess of phosphorus by extraction with a small quantity of alcohol, the entire product was precipitated by water and distilled in a current of steam, whereupon the anthracene hexhydride passed over in small quantity, as a white substance which crystallised from alcohol in laminæ melting at 63°. The residue of the distillation exhausted

with boiling water yielded a solution which, on cooling, deposited white flakes of anthrol,  $C_{14}H_9(OH)$ , identical with that which is obtained by fusing anthracenesulphonic acid with potash (see p. 859).

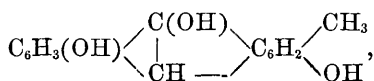
(4.) *Chrysarobin*,  $C_{30}H_{26}O_7$  (Liebermann and Seidler, *Ber.*, **11**, 1603; also Abstr., 1879, 326).—This substance is a constituent of Araroba or Goa powder, and was first extracted therefrom by Attfield, who mistook it for chrysophanic acid, into which indeed it is readily converted by oxidation. When ignited with zinc-dust it yields methylanthracene.

*Acetylchrysarobin*,  $C_{30}H_{22}\overline{AC}_4O_7$  or  $C_{30}H_{21}\overline{AC}_5O_7$ , obtained by heating chrysarobin with acetic anhydride and sodium acetate, forms small yellowish crystals, which melt at  $228-230^\circ$ , and dissolve in alcohol, forming a solution which exhibits a blue fluorescence. By heating with alkalis, it is converted, first into chrysarobin, then into chrysophanic acid.

The oxygen-atom which converts chrysarobin into chrysophanic acid does not enter into either of the hydroxyl-groups of the latter, inasmuch as the oxidation of acetylchrysarobin yields completely acetylated chrysophanic acid. It must therefore be found in the double ketone groups of the chrysophanic acid, and consequently chrysarobin belongs to the group of anthraquinone-derivatives which are reducible in this part of the molecule. Hence its constitution may be represented by the formula—

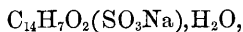


Chrysarobin yields by sublimation, whereby it is for the most part decomposed, a yellow substance crystallising in laminae, and otherwise very much like chrysarobin itself. This substance has the composition  $C_{15}H_{12}O_3$ , and is perhaps the anthranol,



produced by the splitting up of the chrysarobin molecule.

(5.) *Reduction of Anthraquinonesulphonic Acid*.—Anthrol and Anthramine (Liebermann and Hörmann, *Ber.*, **12**, 589; also Abstr., 1879, 653).—Sodium anthraquinonesulphonate,



heated in sealed tubes with very strong hydriodic acid (sp. gr. 1.96) and red phosphorus, is reduced to anthracene dihydride,  $C_{14}H_{12}$ , separable from the sulphonic groups by boiling with water, and from excess of phosphorus by alcohol. By weaker reaction, with acid of 1.7 to 1.8 in a flask, a product is obtained soluble in water, and consisting entirely of sulphonic acids; and on filtering from excess of phosphorus, diluting with water, again filtering at the boiling heat, and removing hydriodic acid so far that the liquid solidifies on cooling to a crystalline mass, *sodium dihydroanthracenemonosulphonate*,  $C_{14}H_{11}SO_3Na (+ \frac{1}{2}H_2O ?)$ , is obtained in snow-white silky asbestos-like needles. The *barium salt*,

(C<sub>14</sub>H<sub>11</sub>SO<sub>3</sub>)<sub>2</sub>Ba, is a white precipitate: the *calcium salt* is more soluble.

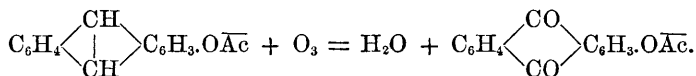
*Sodium anthracenemonosulphonate*, C<sub>14</sub>H<sub>9</sub>.SO<sub>3</sub>Na + 4H<sub>2</sub>O, is obtained by the action of hydriodic acid of sp. gr. 1·7 on the anthraquinonesulphonate for about half an hour at boiling heat, and separates from a strong aqueous solution in a mass of small scales, slightly soluble in water. The barium and lead salts are precipitated in flocks. The lead salt precipitated at the boiling heat is basic; the normal salt separates from the mother-liquor in crystals having the composition (C<sub>14</sub>H<sub>9</sub>.SO<sub>3</sub>)<sub>2</sub>Pb + 2H<sub>2</sub>O. The sodium salt boiled with nitric acid is readily oxidised to anthraquinonesulphonate.

Anthrol, C<sub>14</sub>H<sub>9</sub>(OH) = C<sub>6</sub>H<sub>4</sub> $\begin{array}{c} \text{CH} \\ | \\ \text{CH} \end{array}$ C<sub>6</sub>H<sub>3</sub>(OH).—This compound,

the true phenol of anthracene, is formed, as already observed, by the limited action of hydriodic acid and phosphorus on hydroxyanthraquinone (p. 858), but it is more readily prepared by fusing anthracenesulphonic acid at a very high temperature with potassium hydroxide. On decomposing the melt with dilute hydrochloric acid, the anthrol is obtained in light yellow flocks, insoluble in water, easily soluble, even to deliquescence, in most solvents, as alcohol, ether, and acetone; crystallising from ether in laminæ melting at about 200°. It is insoluble in ammonia, but dissolves in aqueous potash, soda, and baryta, with yellow colour and green fluorescence.\*

*Ethyl-anthrol*, C<sub>14</sub>H<sub>9</sub>.OEt, obtained by heating anthrol with soda-ley and ethyl iodide at 120°, crystallises from dilute alcohol in nearly colourless needles melting at 139—140°, and distilling in small quantities almost without decomposition. On adding fuming nitric acid by drops to a solution of this ethyl-compound in glacial acetic acid, a nitro-derivative is precipitated in yellow needles sparingly soluble in alcohol, insoluble in alkalis, but dissolving in strong sulphuric acid with splendid cherry-red colour. Their composition has not yet been satisfactorily determined, as they gave by analysis numbers intermediate between those required by the formulæ C<sub>16</sub>H<sub>12</sub>(NO<sub>2</sub>)<sub>2</sub>O<sub>3</sub> and C<sub>16</sub>H<sub>11</sub>(NO<sub>2</sub>)<sub>3</sub>O<sub>3</sub>.

*Acetoxyanthraquinone*, C<sub>14</sub>H<sub>7</sub>O<sub>2</sub>.Ac.—Anthrol, like other phenols, cannot be directly oxidised; but its acetyl-derivative dissolved in hot acetic acid is oxidised by chromic acid; and the solution, after slow cooling, gives with water yellow flocks, convertible by recrystallisation into colourless feathery needles of acetoxyanthraquinone, melting at 159°. The reaction is:



\* The compound here described does not agree in properties with either of the two anthrols (α and β) described by Linke (*J. pr. Chem.* [2], 11, 227; this *Journal*, 1875, 1196), which, as well as the two anthracene-monosulphonic acids whence they were said to be obtained, are regarded by Liebermann as impure preparations. There are in fact only two hydroxyanthracenes possible, viz., anthrol and anthranol.

A small quantity of hydroxyanthraquinone is, however, formed at the same time, but may be removed by digesting the product with cold weak soda-ley.

From the preceding results, it may be seen that the isomerism between the two hydroxyanthracenes, anthranol and anthrol, is very well defined, and is clearly indicated by their constitution. Anthranol, whose hydroxyl is situated in the middle carbon-group of anthracene—as follows from its mode of formation—is converted by oxidation into anthraquinone, whereas acetyl-anthrol, whose hydroxyl is situated in the benzene-nucleus, is oxidised to acetoxyanthraquinone.

Anthramine,  $C_{14}H_9.NH_2 = C_6H_4 \begin{array}{c} \diagup CH \\ | \\ CH \diagdown \end{array} C_6H_3.NH_2$ , is formed by

heating 1 pt. anthrol with 3 pts. acetamide for eight hours at  $280^\circ$ , or with alcohol and ammonia at  $170^\circ$ . From alcohol, in which it dissolves at boiling heat with yellow-brown colour and green fluorescence, it separates in thin yellow laminæ resembling mosaic gold. It melts at  $236-237^\circ$ , and sublimes at a higher temperature in yellow laminæ. It dissolves but sparingly in most solvents; the acetic acid solution is coloured red by nitric acid. With arsenic acid in the cold, it forms a colourless arsenate, which when heated melts to a mass having a fine blue colour. The *hydrochloride*,  $C_{14}H_{11}N.HCl$ , is best obtained by boiling anthramine with strong hydrochloric acid and diluting the hot solution with 4 pts. water, the salt then separating on cooling in glittering colourless laminæ.

*Acetylanthramine*,  $C_{14}H_9.NHAc$ , is formed on dissolving anthramine in a large quantity of acetic anhydride, and separates on cooling in silvery laminæ. After purification by recrystallisation from alcohol or glacial acetic acid, it melts at  $240^\circ$ . The alcoholic solution exhibits blue fluorescence.

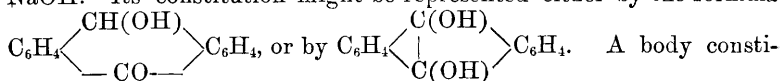
*Acetylamidanthraquinone*,  $C_{14}H_7O_2.NHAc$ , is easily formed by oxidising acetylanthramine dissolved in boiling acetic acid with the calculated quantity of chromic acid, and is precipitated by water in yellow flocks, which must be dried and again acetylated, to replace any acetyl that may have been removed during the oxidation. It crystallises from glacial acetic acid in colourless needles, which appear to contain acetic acid, since they turn yellow when dried over the water-bath.

*Amidanthraquinone*,  $C_{14}H_7O_2.NH_2$ , formed by boiling the preceding compound with alcoholic potash, is precipitated from the resulting orange-coloured solution by water, and crystallises from glacial acetic acid in brown-orange needles melting at  $302^\circ$ . The solutions of these two compounds, unlike those of the corresponding anthracene-derivatives, are not fluorescent, in which respect they conform to the general law of fluorescence in the anthracene series (Liebermann, *Ber.*, **13**, 913; *Chem. Soc. J.*, 1880, Abstr., 665).

## Part II. THE ALKYLISED REDUCTION-PRODUCTS OF ANTHRAQUINONE.

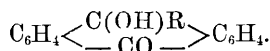
—(1.) *The Alkylloxanthranols and their Derivatives* (Liebermann and Landshoff, *Ber.*, **14**, 452—462; also Abstr., 1881, 608).—*Oxanthranol* or *Anthraquinol*,  $C_{14}H_{10}O_2$ , is best prepared by treating 1 pt. anthra-

quinone moistened with a very small quantity of alcohol with 2 pts. zinc-dust and 30 pts. of a soda-solution containing 50 p. c. NaOH. Its constitution might be represented either by the formula



A body constituted according to the first of these formulæ should yield only one acetyl or alkyl-derivative, whereas the structure represented by the second admits of the formation of two such derivatives. Experiments with acetic chloride did not lead to any decisive result, but the action of alkyl iodides on oxanthranol gave rise only to monalkyl-derivatives: hence it may be inferred that the constitution of oxanthranol is correctly represented by the first of the above formulæ.

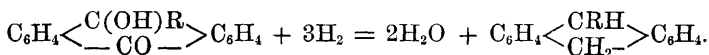
The general formula of these monalkyl-derivatives is—



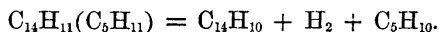
They are prepared by boiling a solution of oxanthranol in potash with an alkyl bromide or iodide (for details see this Journal, 1881, Abstr., 109, 608).

*Ethylloxanthranol*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{C(OH)Et} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{C}_6\text{H}_4$ , crystallises in needles or prisms belonging to the rhombic system and melting at  $107^\circ$ . Heated with acetic chloride, it yields a substance,  $\text{C}_{20}\text{H}_{18}\text{O}_4 = \text{C}_{18}\text{H}_{14}\text{O}_2 + (\text{C}_2\text{H}_3\text{O})_2\text{O} - \text{H}_2\text{O}$ , which crystallises from light petroleum in needles melting at  $84^\circ$ . *Isobutylloxanthranol*,  $\text{C}_{14}\text{H}_9(\text{C}_4\text{H}_9)\text{O}_2$ , crystallises from benzene or from light petroleum in needles, from alcohol in thick prisms; it is less soluble than the ethyl-compound. *Amyl-oxanthranol*,  $\text{C}_{14}\text{H}_9(\text{C}_5\text{H}_{11})\text{O}_2$ , forms limpid, tabular, monoclinic crystals,  $\infty\text{P} \propto .0\text{P}$ .  $\infty\text{P}$ , melting at  $125^\circ$ , and behaving with solvents like the butyl-compound. Treated with acetic chloride it undergoes simple dehydration, yielding the compound  $\text{C}_{19}\text{H}_{18}\text{O} = \text{C}_{19}\text{H}_{20}\text{O}_2 - \text{H}_2\text{O}$ , which is also formed by treating it with strong sulphuric acid at ordinary temperatures; but at higher temperatures hydrogen is likewise eliminated, and a substance is obtained having the composition  $\text{C}_{19}\text{H}_{14}\text{O} = \text{C}_{19}\text{H}_{20}\text{O}_2 - \text{H}_2\text{O} - 2\text{H}_2$ . This latter substance is converted by oxidation with chromic acid into anthraquinone-carboxylic acid,  $\text{C}_{18}\text{H}_8\text{O}_4 = \text{C}_{14}\text{H}_7\text{O}_2.\text{COOH}$ , and by prolonged boiling of its concentrated boiling solution in glacial acetic acid with hydriodic acid of sp. gr. 1.9, into triphenylmethane. *Methyl-oxanthranol*,  $\text{C}_{14}\text{H}_9\text{MeO}_2$ , crystallises in colourless laminæ melting at  $187^\circ$ ; its alcoholic solution exhibits a fine blue fluorescence. This compound differs from its homologues in many respects, not being altered by zinc-dust and alkali; and being converted by hydriodic acid and phosphorus into anthracene dihydride,  $\text{C}_{14}\text{H}_{12}$ , with separation of methyl.

*Alkyl-anthradihydrides*.—These compounds are formed by the action of hydriodic acid and phosphorus on all the alkyl-oxanthranols—except the methyl-compound—as shown by the equation—

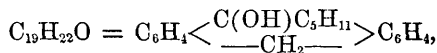


The *ethyl-compound*,  $C_{14}H_{11}Et$ , thus prepared is a liquid boiling at  $320-323^\circ$  (corr.), and having a density of  $1.049$  at  $18^\circ$  (referred to water at the same temperature). Chromic acid dissolved in glacial acetic acid oxidises it to anthraquinone. Passed over pumice at a red heat it yields anthracene. Its solution in glacial acetic acid treated with nitric acid free from nitrous products, yields a finely crystallised trinitro-derivative,  $C_{14}H_8(NO_2)_3Et$ , which melts with evolution of gas at  $130^\circ$ . *Isobutyl-anthradihydride* passed over zinc-dust at a low red-heat yields pure anthracene. *Amyl-anthradihydride* is much more viscid than the ethyl-compound. It has a density of  $1.031$  at  $18^\circ$  (water at  $18^\circ = 1$ ), and boils, with decomposition, at about  $350^\circ$ , giving off combustible gases and vapours having an amyl odour. If the distillation be then interrupted, and the whole left to cool, both residue and distillate deposit crystals of anthracene:

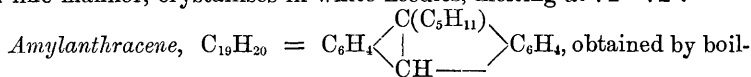


*Alkylloxanthranyl chlorides*,  $C_6H_4 \begin{smallmatrix} \text{CRCl} \\ \text{—CO—} \end{smallmatrix} C_6H_4$ , are formed by the action of  $PCl_5$  on the corresponding oxanthranols. The *ethyl-compound* forms transparent colourless rhombic crystals melting at  $88-89^\circ$ . The *butyl-compound* forms tabular crystals melting at  $78^\circ$ , and coloured red by nitric acid. The *amyl-compound* forms large yellowish monoclinic crystals,  $\infty P . P \infty . 0P$ . Axes  $a : b : c = 1.266 : 1 : 2.752$ ;  $\beta = 68^\circ 23'$ .

(2.) *The Alkyl-hydranthranols and Alkyl-anthracenes* (Liebermann and Tobias, *Ber.*, **14**, 795).—The alkyl-hydranthranols are formed, as products of further reduction, in the preparation of the alkyl-oxanthranols (p. 861). The *amyl-compound*,



which is extremely soluble, was separated from the product of the action of zinc-dust and soda on anthraquinone by exposure to prolonged winter-cold, whereupon it separated as a crystalline mass; and on pressing this mass, dissolving it in alcohol, treating the alcoholic solution with water, and repeating this treatment on the crystals thereby separated, the amyl-hydranthranol was at length obtained in groups of white needles melting at  $73-74^\circ$ . Its alcoholic solution exhibits a faint fluorescence. The *isobutyl-compound*,  $C_{18}H_{20}O$ , obtained in like manner, crystallises in white needles, melting at  $71-72^\circ$ .



ing amyhydranthranol with hydrochloric acid and alcohol, crystallises from alcohol in thin very long needles, having a sea-green colour and blue fluorescence, and melting at  $59^\circ$ . It is easily soluble in hot, sparingly in cold alcohol, very easily in benzene, light petroleum, carbon bisulphide, and chloroform. It forms a *picrate* which crystallises in groups of brown-red needles melting at  $115^\circ$ , and is easily resolved into its constituents by water or ammonia. By oxidation with chromic acid, it is completely converted into amyloxanthranol.

*Amylbromanthracene*,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C}(\text{C}_6\text{H}_{11}) \\ | \\ \text{CBr} \text{---} \end{array} \diagdown \text{C}_6\text{H}_4$ , obtained by the action

of bromine on amylanthracene dissolved in carbon bisulphide, crystallises from alcohol in needles melting at  $76^\circ$ ; the alcoholic solution is strongly fluorescent. Its *picrate* forms orange-coloured needles melting at  $110^\circ$ . Chromic acid oxidises it completely to anthraquinone.

*Amylchloranthracene*,  $\text{C}_{19}\text{H}_{19}\text{Cl}$ , obtained by passing chlorine into amylanthracene dissolved in chloroform, crystallises in light yellow needles melting at  $70\text{--}71^\circ$ ; its solution has a blue fluorescence. The *picrate* forms red needles melting at  $108^\circ$ .

*Isobutylanthracene*,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C}(\text{C}_4\text{H}_9) \\ | \\ \text{CH} \text{---} \end{array} \diagdown \text{C}_6\text{H}_4$ , prepared like the amyl-

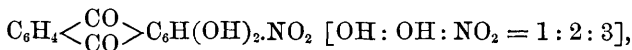
compound, forms fluorescent crystals melting at  $57^\circ$ . Its *picrate* crystallises in long brown-red needles.

*Ethyl-anthracene*,  $\text{C}_{14}\text{H}_9\text{Et}$ , prepared by boiling an alcoholic solution of ethyl-hydranthranol with hydrochloric acid, precipitating with water, boiling the oil thereby separated with a saturated solution of picric acid, and decomposing the resulting *picrate* with ammonia, crystallises in spherical groups of large laminae melting at  $60\text{--}61^\circ$ . Its *picrate* melts at  $120^\circ$ .

The paper concludes with theoretical speculations respecting the formation, constitution, and reactions of these several compounds, which do not admit of abstraction. H. W.

**Preparation of Alizarin-orange.** By S. F. SIMON (*Ber.*, 15, 692—694).—On adding a 20 per cent. soda solution to the dinitro-hydroxyanthraquinone described by the author (*Abstr.*, 1881, 608), a deep-red solution is formed, from which, on evaporation, a dark-red sodium salt separates out in a flocculent mass. On decomposing this with hydrochloric acid, it gives the free acid in the form of orange-golden, glistening needles (m. p.  $244^\circ$ ). It is identical with mononitroalizarin or alizarin-orange, and is formed from dinitroalizarin by the displacement of a nitro- by a hydroxyl-group. Baryta and lime-water act on dinitroalizarin in a similar manner.

As the amidoalizarin from the mononitroalizarin gives an ethenyl compound, the amido- and hydroxyl-group are in contiguous position, and thus the nitroalizarin has the constitution



and the dinitroalizarin, which yields the mononitro-compound, has the constitution  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \\ | \\ \text{CO} \end{array} \diagdown \text{C}_6\text{H}(\text{OH})(\text{NO}_2)_2 \quad [\text{NO}_2 : \text{OH} : \text{NO}_2 = 1 : 2 : 3]$ .

On heating the silver salt of dinitrohydroxyanthraquinone with ethyl iodide, the ethyl ether,  $\text{C}_{14}\text{H}_9\text{O}_2(\text{NO}_2)_2.\text{OEt}$ , is obtained. It crystallises in fine needles (m. p.  $158^\circ$ ); it is not attacked by dilute soda solution, but a concentrated solution converts it into alizarin-orange.

V. H. V.



**Dichlorocamphor.** By P. CAZENEUVE and DIDELOT (*Compt. rend.*, **94**, 1058—1059).—Dichlorocamphor (this vol., p. 738) is insoluble in water, but imparts to it its peculiar odour. When placed on the surface of water, it exhibits gyratory movements, similar to those of camphor. It is insoluble in cold, but readily soluble in hot alcohol, in chloroform, carbon bisulphide, and ether. The ethereal solution crystallises with difficulty, and the ether appears to form a molecular combination with the dichlorocamphor. The latter, unlike camphor, is insoluble in acetic acid. It combines with aldehyde in aqueous solution, forming a liquid heavier than water, but does not liquefy when triturated with chloral hydrate. Its sp. gr. is 4.2; it melts at 96°, and solidifies at 95°, but remains soft and pasty below 70°. The monochloro-camphor described by Wheeler melts at 95°. The rotatory power of dichlorocamphor for  $[\alpha]_D = +57.3^\circ$ , and is constant in both alcohol and chloroform. Dichlorocamphor crystallises well only from alcohol, in right rhombic prisms, with brachydiagonal domes, and with difficult cleavage in two directions parallel with the faces of the prism. When the crystals form rapidly, the faces of the prism are much elongated, and the crystals are long friable needles; when, on the other hand, they form very slowly, the prismatic faces are but little developed, and the crystals have an octohedral appearance.

C. H. B.

### Two Isomeric Dibromocamphors and Monobromocamphor.

By J. KACHLER and F. V. SPITZER (*Monatsh. Chem.*, **3**, 205—221).—Monobromocamphor, discovered by Perkin in 1865, forms colourless monoclinic crystals, melts at 76°, boils without decomposition at 274°, and is reconverted into camphor by the action of alcoholic potash, or by heating it in alcoholic solution with sodium-amalgam. R. Schiff, by heating it with nitric acid, obtained a crystalline substance,  $C_{10}H_{14}NO_3$ , which he regarded as bromonitrocarnphor.

By the further action of bromine, monobromocamphor is converted into dibromocamphor, the statements respecting which by different authors exhibit considerable divergencies, due, as the following experiments will show, to the existence, not previously suspected, of two isomeric dibromocamphors ( $\alpha$  and  $\beta$ ).

$\alpha$ -Dibromocamphor is obtained by heating 1 mol. monobromocamphor with 1 mol. bromine in sealed tubes at 120°, and separates from the resulting syrupy liquid as a crystalline mass, which dissolves with moderate facility in alcohol, and is deposited therefrom in prismatic needles melting at 61°.

$\beta$ -Dibromocamphor is obtained by heating monobromocamphor with bromine in the ratio of  $C_{10}H_{15}BrO$  to  $3Br$  for six or eight hours in sealed tubes at 120—125°, whereby a brown syrup is formed, which slowly deposits crystals, and when mixed with absolute alcohol, immediately yields a pulverulent crystalline mass, only slightly soluble in alcohol, even at the boiling heat, and separating from the solution in thick rectangular plates, having also the composition  $C_{10}H_{14}Br_2O$ , but melting at 114—115°. The mother-liquor contains monobromocamphor. The  $\beta$ -modification of dibromocamphor is also formed by heating the  $\alpha$ -modification with 2 at. bromine in sealed tubes at 120—125° for six to eight hours. A red laminar sublimate then forms

in the upper part of the tube, apparently consisting of an unstable compound of  $C_{10}H_{14}Br_2O$  with bromine, which it gradually gives off, leaving  $\alpha$ -dibromocamphor (m. p.  $61^\circ$ ). The greater part of the product, however, is a brown-red viscid liquid, which, when mixed with alcohol, immediately deposits a crystalline powder, having, after recrystallisation from alcohol, the composition  $C_{10}H_{14}Br_2O$ , and melting at  $114$ – $115^\circ$ , which is the characteristic melting point of  $\beta$ -dibromocamphor.

The differences between the two modifications of dibromocamphor are shown in the following table:—

	$\alpha$ .	$\beta$ .
Crystalline form.....	Rhombic: $a : b : c = 0.7925 : 1 : 0.5143$ . Observed faces, $\infty P_{\infty}^{\alpha}$ , $P_{\infty}^{\alpha}$ , $P_{\infty}^{\alpha}$ , $\infty P$ .	Rhombic: $a : b : c = 0.9501 : 1 : 1.35206$ . Observed faces $\infty P$ , $P_{\infty}^{\beta}$ , $\infty P_{\infty}^{\beta}$ .
Solubility .....	Very soluble in alcohol, ether, ethylacetate, and light petroleum.	Sparingly soluble in alcohol, ether, ethyl acetate, and light petroleum.
Alcoholic potash .....	Monobromocamphor, and finally camphor.	Oil smelling like turpentine, and distilling between $150^\circ$ and $230^\circ$ .
Nascent hydrogen from sodium-amalgam with dilute alcohol.	Monobromocamphor; finally camphor.	Hydroxycamphor, $C_{10}H_{15}(OH)$ , boiling at $258$ – $260^\circ$ .
Nascent hydrogen from sodium-amalgam and ether saturated with hydrochloric acid, in ethereal solution	Camphor .....	Camphor.
Sodium and carbonic anhydride	Camphocarboxylic acid, $C_{11}H_{16}O_3$ ,* melting at $123$ – $124^\circ$ .	Resinous masses.
Phosphorus pentachloride..	No reaction .....	No reaction.
Fuming nitric acid .....	Nitrogen and a brominated oil.	Dibromomononitrocamphor, $C_{10}H_{13}Br_2NO_3$ , m. p. $126^\circ$ .

H. W.

**Crystalline Forms of Dibromocamphor.** By V. v. ZEPHAROVICH (*Monatsh. Chem.*, **3**, 231–236).—The two modifications of this compound,  $\alpha$  melting at  $60$ – $61^\circ$ ,  $\beta$  at  $114$ – $115^\circ$  (*supra*), both crystallise in the rhombic system, with the following axial ratios—

$$a : b : c = 0.7925 : 1 : 0.5143; \quad \beta \quad 0.9501 : 1 : 0.5206,$$

\* Misprinted in the original  $C_{20}H_{32}O_6$ .

and separate from alcoholic solution in crystals exhibiting the combination  $\infty P\infty . P\infty . \infty P$ . The  $\beta$ -crystals, from predominance of the brachypinacoid, appear as rectangular tablets with bevelled edges; they are mostly elongated in the direction of the brachydiagonal and at most 2 mm. broad by 1 mm. thick. Rarely and with very small development occur the faces  $P\infty$ ,  $\infty P^2$ , and  $P$ . Cleavage indistinct parallel to  $OP$ .

The following table exhibits a comparison of the most important angles in the two modifications:—

	$P\infty : P\infty$ .	$P\infty : P\infty$ .	$\infty P : \infty P$ .	$P : \infty P\infty$ .
$\alpha$ .	$54^\circ 26'$	$65^\circ 58'$	$76^\circ 47\frac{1}{2}'$	$66^\circ 40'$
$\beta$ .	$55^\circ 0'$	$57^\circ 26'$	$87^\circ 4'$	$65^\circ 27'$

In both modifications the plane of the optic axes is parallel to  $OP$ .

H. W.

**Galangin and Alpinin.** By E. JAHNS (*Ber.*, 14, 2807—2811).—As already stated (this vol., 209), these two bodies are found in *galanga* root together with campheride.

*Galangin*,  $C_{15}H_{10}O_5$ , crystallises from absolute alcohol in pale yellow, six-sided tablets, or in flat prisms containing  $\frac{1}{2}$  mol. of alcohol of crystallisation, which they lose at  $100$ — $110^\circ$ . It crystallises from aqueous alcohol in yellowish-white needles, having the composition  $C_{15}H_{10}O_5 + H_2O$ , losing the water at  $130$ — $140^\circ$ . It is insoluble in water, easily soluble in ether, and sparingly in benzene and boiling chloroform. It dissolves in 68 parts of alcohol (90 per cent.), and in 34 parts of absolute alcohol. In its reactions with alkalis and ferric chloride, it resembles campheride; in alcoholic solution, lead salts produce an orange-yellow precipitate of  $C_{15}H_8O_5Pb$ . Strong sulphuric acid dissolves it, forming a yellow non-fluorescent solution, and fuming sulphuric acid gives a similar solution; whilst with campheride it gives a green or red solution. *Triacetogalangin*,  $C_{15}H_7O_5Ac_3$ , obtained by heating galangin with sodium acetate and acetic anhydride, forms colourless needles, insoluble in water, but soluble in aqueous alcohol (m. p.  $140$ — $142^\circ$ ). *Dibromogalangin*,  $C_{15}H_7Br_2O_5$ , formed by adding bromine (1 part) to galangin (2 parts), is insoluble in water, and only sparingly soluble in alcohol. A more highly brominated product is also formed, which is more easily soluble. Nitric acid converts galangin into benzoic and oxalic acids; these products are also obtained by fusion with potash, together with a phenol.

By repeated fractional crystallisation from aqueous alcohol (70—80 per cent.), a small quantity of *alpinin*,  $C_{17}H_{12}O_6$ , has been obtained; it crystallises in pale-yellow needles (m. p.  $172$ — $174^\circ$ ). It exhibits a great resemblance to campheride in its properties and reactions.

P. P. B.

**Chemical Constituents of Stereocaulon Vesuvianum.** By M. COPPOLA (*Gazzetta*, 12, 19—27).—The author examined this lichen some time ago (Abstr., 1880, 382), and found in it succinic acid, whilst Paternò by treating it with ether, obtained atranoric acid (*ibid.*, 551). In order to explain this apparent discrepancy, the author has

again taken up the investigation, first of all exhausting the lichen with ether, and then treating it with milk of lime. The residue left on evaporating the ethereal solution, was separated into two portions by fractional crystallisation from chloroform: the more soluble of these is a mixture of brilliant well-formed crystals with a white crystalline substance; both forms appear to be atranoric acid. The crystals (m. p.  $191^{\circ}$ ) were measured by Scacchi, and found to be trimetric orthogonal (orthorhombic).

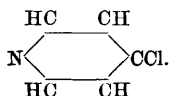
$a : b : c = 1 : 0.3983 : 0.3064$ . Two planes of cleavage.

The portion less soluble in chloroform is a fine powder, which, under the microscope, is seen to consist of very minute needles; it is not homogeneous, however, but appears to be a mixture of two substances, which may be separated to a certain extent by treatment with boiling chloroform in quantity insufficient to dissolve the whole. The portion remaining undissolved, after being crystallised from absolute alcohol, forms microscopic prisms with rectangular base; it decomposes at  $225^{\circ}$ , without melting.

When the lichen which has been exhausted with ether is treated with milk of lime, it yields a solution containing calcium succinate. The succinic acid was identified by the usual reactions, and by the analysis of the free acid and of its barium compound. C. E. G.

### Conversion of Pyrroline into Pyridine. (Preliminary Notice.)

By G. CIAMICIAN and M. DENNSTEDT (*Gazzetta*, 1882, 154).—By the action of chloroform or bromoform on potassium-pyrroline, two bases are obtained, having respectively the formulæ  $C_5H_4ClN$  and  $C_5H_4BrN$ , and identical in boiling point, &c., with the corresponding compound obtained directly from pyridine. Nascent hydrogen transforms chloropyridine into a hydrochloropyridine, and removes the bromine from bromopyridine, producing a mixture of pyridine and hydro-pyridine. The authors consider it most probable that the halogen in these bases stands in the para-position to the nitrogen-atom, *e.g.*:—



H. W.

### Monobromopyridine. By L. DANESI (*Gazzetta*, 1882, 150—151).

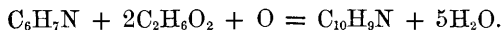
—This compound, discovered by Hofmann in 1879 (*Ber.*, 12, 990), is prepared by heating pyridine hydrochloride with bromine in sealed tubes at about  $200^{\circ}$ ; distilling the contents in a current of steam, to expel dibromopyridine formed at the same time; then adding potash to alkaline reaction; distilling again; mixing the oily distillate with excess of hydrochloric acid; and repeating the same course of treatment in order to expel the last portions of dibromopyridine. From the resulting liquid, after addition of potash, ether extracts the monobromopyridine, together with traces of the dibromo-compound and unaltered pyridine, which may be removed by fractional distillation, the liquid passing over at  $169$ — $170^{\circ}$  being the pure monobromo-derivative.

Monobromopyridine thus prepared is a liquid slightly soluble in water, to which it imparts an alkaline reaction. It dissolves readily in hydrochloric acid, and platinic chloride throws down from the solution the platinochloride  $(C_5H_4BrN, HCl)_2, PtCl_4$ , which is slightly soluble in water, and is decomposed by pressure between the fingers, emitting the odour of the free base. The mother-liquors of the platinochloride deposit, on slow evaporation, some very fine crystals, which have not yet been examined.

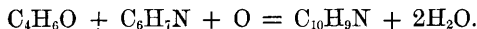
The following note is added by Cannizzaro:—The bromopyridine prepared as above is identical with that which Ciamician and Dennstedt obtained by the action of bromoform on pyrroline, as shown by the agreement of the boiling points and other physical characters, and of the crystalline forms of the platinochlorides.

H. W.

**A Homologue of Quinoline.** By O. DOEBNER and W. v. MILLER (*Ber.*, **14**, 2812—2817).—This base is obtained by heating to about  $180^\circ$  a mixture of 30 parts of glycol, 14 of aniline, 14 of nitrobenzene, and 38 of strong sulphuric acid in a vessel connected with a reversed condenser. The product of the reaction, after removal of nitrobenzene by passing steam through it, is treated with caustic soda, and the base driven over by steam. On fractionating this distillate, the chief portion boils at  $238\text{--}239^\circ$ , and consists of a base having the composition  $C_{10}H_9N$ . It is a colourless highly refractive liquid, having an odour resembling that of quinoline. Its salts are easily soluble in water; the chromate is a well-defined crystalline salt, and the aurochloride is obtained in the form of yellow crystals. The platinochloride,  $(C_{10}H_9N, HCl)_2, PtCl_4$ , forms orange-yellow needles, soluble in hot water, from which it crystallises in reddish-orange prisms. The formation of this base may be represented as follows:—



The composition of this base, also the fact that glycol has been shown to yield aldehyde and crotonaldehyde (Nevolé, *Bull. Soc. Chim.*, **25**, 289), lead the authors to interpret its formation as arising from the presence of crotonaldehyde, thus:—



This supposition receives considerable support, from the fact that this same base is obtained by heating 80 parts of paraldehyde, 40 of aniline, 45 of nitrobenzene, and 100 of strong sulphuric acid.

P. P. B.

**Quinoline Tartrate and Salicylate.** By G. FRIESE (*Ber.*, **14**, 2805—2806).—The author has analysed the “chinolinum tartaricum” prepared synthetically by Messrs. Hofmann and Schötinsuck and used as a febrifuge; the composition of this preparation is expressed by the formula  $2C_9H_7N + 4C_6H_6O_6$ . The quinoline prepared from this salt was found to boil at  $235.65^\circ$  (corr.), and for its identification the author recommends the sparingly soluble and beautifully crystalline chromate. The tartrate, when decomposed by heat, yields quinoline and an organic acid.

*Quinoline salicylate* is a reddish-grey slightly crystalline powder, and has the composition  $C_9H_7N + C_7H_6O_3$ . P. P. B.

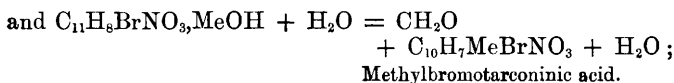
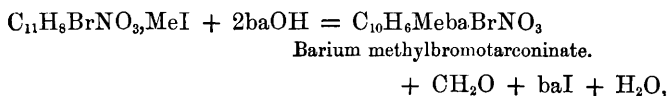
**$\alpha$ -Hydroxyquinoline.** By K. BEDALL and O. FISCHER (*Ber.*, **15**, 683—684).—The authors have shown (this vol., 413) that the hydroxyl-group in  $\alpha$ -hydroxyquinoline is in the same position as the amido- and nitro-groups of the amido- and nitro-quinoline described by Königs; and that with potassium cyanide, quinolinesulphonic acid gives a meta-cyanoquinoline, from which is produced a carboxyl acid identical with that obtained by Skraup and Schlosser from metanitrobenzoic acid. In the present communication it is shown that the cyanogen compound consists of two meta- and probably ortho-cyanoquinolines.

These arise from two quinolinesulphonic acids, which on account of the similarity of their crystalline form and solubility, are not separable; the authors propose to subject them to more minute examination. As the authors'  $\alpha$ -hydroxyquinoline is volatile in a current of steam, it would appear to be the ortho-compound; a view which is further confirmed by the identity of this  $\alpha$ -hydroxyquinoline with that obtained by Skraup from orthonitro- and orthamido-phenol.

V. H. V.

**Cotarnine.** By E. v. GERICHTEN (*Annalen*, **212**, 165—202).—In a former paper (this volume, p. 331) the author described a series of bodies produced by the action of bromine on an aqueous solution of bromotarconine hydrochloride,  $C_{11}H_8BrNO_3.HCl$ , all of which are derivatives of pyridine, and for the most part closely related to Hofmann's dibromopyridine. The experiments described in the present paper were made with the view of throwing further light on the constitution of these bodies, and of cotarnine itself.

By the action of barium hydroxide on methylbromotarconium iodide, or the corresponding hydrochloride, formaldehyde,  $CH_2O$ , is evolved, and methylbromotarconinic acid is produced—



and the homologous ethyl-compound treated in like manner, yields formaldehyde and ethyl-bromotarconinic acid.

The action of hydrogen chloride on methyl-bromotarconinic acid gives rise to the hydrochloride of a non-azotised acid, tarconic acid,  $C_{10}H_7NO_3$ :



and the same body is formed by heating ethyl-bromotarconinic acid with hydrochloric acid. This result shows that in the dimethylisation of methylbromotarconinic acid, the methyl-group removed is the same as that which, in the molecule of the methiodide, was directly attached to the bromotarconine.

The formation of the bromotarconine derivatives previously described by the author (*C. J.*, 1881, Abstr., 445) exhibits a certain analogy to that of methyl-bromotarconinic acid, tarconic acid, &c. When bromotarconine is heated with water at  $140^{\circ}$ , there is formed, together with the colouring matter called *cupronine* (*loc. cit.*), a non-brominated body, *tarnine*,  $C_{11}H_9NO_4$ , the reactions of which are very similar to those of bromotarconine. Its formation (as hydrobromide) is represented by the equation  $C_{11}H_9BrNO_3 + H_2O = C_{11}H_9NO_4, HBr$ . Bromotarconine heated with hydrochloric acid yields a body,  $C_{20}H_{16}N_2O_6$ , called *nartine*. Its formation takes place as shown by the equation:—



The following are a few details respecting the preparation and properties of the bodies above mentioned:—

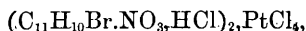
*Methylbromotarconium iodide*,  $C_{11}H_9BrNO_3, MeI$ , prepared by heating anhydrous bromotarconine for two hours on the water-bath with methyl iodide, may be extracted from the product with water, and obtained by concentrating the aqueous solution in long yellow anhydrous needles. It dissolves readily in cold, very easily in warm water, also in alcohol, but is insoluble in ether. It turns brown at  $170^{\circ}$ , and melts at  $203\text{--}204^{\circ}$  to a greenish-black liquid, giving off methyl iodide and formaldehyde, and yielding a crystalline sublimate of trioxymethylene. On cooling the melt solidifies to a black mass, which has a copper-coloured metallic reflex, and dissolves in water with deep green colour; and on mixing this solution with sodium carbonate, bromotarconine is precipitated in a mass of slender needles. At the same time formaldehyde is produced (indicated by its odour), hydrogen bromide is given off, and basic salts of more highly constituted bases are formed, to which the change of colour appears to be due. The *chloride*, obtained by digesting the solution of the iodide with silver chloride, yields with platinic chloride a yellow crystalline precipitate of the salt  $(C_{11}H_9BrNO_3, MeCl)_2, PtCl_4$ . By decomposing the iodide in aqueous solution with silver oxide, a reddish strongly alkaline liquid is obtained, which when slowly evaporated yields the base,  $C_{11}H_9BrNO_3, MeOH$ , in small orange-red needles, usually aggregated in spherical groups.

*Ethylbromotarconium iodide*,  $C_{11}H_9BrNO_3, EtI$ , prepared like the methyl-compound, crystallises from concentrated aqueous solution in tufts of very long, shining, light yellow needles, melting at  $205\text{--}206^{\circ}$ .

The combination of the higher alkyl iodides with bromotarconine takes place with much greater difficulty, and is attended with the formation of larger quantities of resinous products. The amyl compound crystallises from aqueous solution in geodes of shining yellow needles.

*Methylbromotarconinic acid*,  $C_{11}H_{10}BrNO_3$ , is formed, with evolution of formaldehyde, during the evaporation of an aqueous solution of methylbromotarconium hydroxide, but it is more readily prepared by the use of baryta-water, as above indicated (p. 869). It crystallises in short, yellow, brittle, shining prisms, which give off their water

(2 mols.) at  $100^{\circ}$ . It is nearly insoluble in cold, only slightly soluble in hot water, dissolves with moderate facility in hot, less readily in cold alcohol, and is insoluble in ether. It gradually darkens at  $215^{\circ}$ , and melts at  $223^{\circ}$ . It is indifferent to vegetable colours, and forms saline compounds both with bases and with acids, yielding with certain mineral acids splendidly crystallised salts. The *hydrochloride* crystallises in tufts of needles or in short thick prisms, dissolves easily in cold water, and forms with platinic chloride a yellow precipitate made up of fine needles, having the composition



dissolving with moderate facility in dilute hydrochloric acid. Methyl-bromotarconinic acid dissolves in sodium carbonate and very easily in caustic alkalis. Its *sodium salt* separates from a somewhat concentrated solution in stellate groups of long light-yellow needles, which when heated turn red, and then decompose with evolution of pyridine. The aqueous solution of the acid forms with cupric salts a greenish-yellow bulky precipitate of the salt  $(C_{11}H_9BrNO_3)_2Cu$ , easily soluble in excess of mineral acids, but insoluble in acetic acid; it is not precipitated by barium chloride or nitrate; but gives with barium hydroxide a deep yellow precipitate of the salt  $(C_{11}H_9BrNO_3)_2Ba$ . The aqueous solution is not precipitated by lead acetate, normal or basic, or by silver nitrate. With ferric chloride, at ordinary temperatures, it forms a finely divided red-brown precipitate, which on adding excess of ferric chloride, or on very gentle heating, turns to deep violet (like the salicylic acid reaction), changing to brown on stronger heating.

*Ethylbromotarconinic acid*,  $C_{12}H_{12}BrNO_3$ , prepared like the methyl-compound, is somewhat more soluble in hot water, and crystallises in yellow shining needles containing  $2H_2O$ . It dissolves very sparingly in cold, with moderate facility in hot water, easily in alcohol, but is insoluble in ether. Its hot aqueous solution is perfectly neutral. With acids and with bases, it reacts just like the methyl-compound, dissolving in mineral acids and in acetic acid. Its *hydrochloride* crystallises in furcate groups of slender yellowish-white needles, easily soluble even in cold water. The *platinocchloride* crystallises in slender yellow needles, easily soluble in water acidulated with hydrochloric acid. The acid dissolves easily in strong sulphuric acid with yellow colour, changing to brown-red on heating. Its *copper salt*,



prepared like the corresponding methyl-compound, is a yellow-green flocculent precipitate. With baryta-water, it forms a yellow precipitate sparingly soluble in hot water. With ferric chloride, it reacts like the methyl-compound.

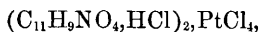
*Tarconic Acid*,  $C_{10}H_7NO_3$ .—The hydrochloride of this body is formed on heating methyl- or ethyl-bromotarconinic acid with strong hydrochloric acid in a sealed tube at  $150$ – $160^{\circ}$  (p. 869), and separates on cooling in stellate groups of long, brittle, brown-yellow prisms. This salt is sparingly soluble in cold, more freely in boiling water, insoluble



in acids, and only slightly soluble in hot alcohol, easily in sodium hydroxide or carbonate, forming a brown-yellow solution.

*Tarnine*,  $C_{11}H_9NO_4$  or  $C_{22}H_{18}N_2O_8$ .—This base, and cupronine,  $C_{20}H_{18}N_2O_6$ , are formed, as hydrobromides, by heating bromotarconine with water in a sealed tube at  $130^\circ$  for four hours. The tube then becomes filled with long yellow crystals of tarnine hydrobromide and dark-coloured needles of cupronine hydrobromide, blue-green by transmitted light, and having a splendid coppery lustre by reflected light. On opening the tube, carbon dioxide escapes. The two hydrobromides may be easily separated by digestion with a large quantity of cold water, which dissolves only the tarnine salt; and the resulting solution mixed with sodium carbonate deposits the base in gelatinous brown masses of very slender needles.

Tarnine is moderately soluble in hot water, very easily in dilute alcohol, insoluble in ether. It crystallises from its solutions in long very thin orange-red silky needles, which give off their water in the exsiccator and assume a scarlet colour. It does not melt at  $290^\circ$ . With acids, it forms well-crystallised salts, which, however, are partially decomposed by water. The *hydrochloride* forms stellate groups of pale yellow, slender needles, easily soluble in cold water, less easily in cold alcohol, readily in hot alcohol. The *platinochloride*,



is a precipitate consisting of light yellow microscopic needles, sparingly soluble in cold water, easily and with decomposition in warm water, easily also in hot alcohol and in warm strong hydrochloric acid, from which latter it crystallises in long needles.

Tarnine is precipitated from its solution by alkaline carbonates and hydroxides (distinction from nartine). Heated with soda-lime, it gives off a distinct odour of pyridine. In strong sulphuric acid, it dissolves without coloration, the solution when heated turning brown-red. Heated with strong hydrochloric acid at  $160^\circ$ , it gives off carbonic oxide, and is converted into nartine.

The yield of tarnine from bromocotarconine is scarcely 10 per cent. Its formation is represented by the equation  $C_{11}H_9BrNO_3 + H_2O = HBr + C_{10}H_9NO_4$ .

*Cupronine*,  $C_{20}H_{18}N_2O_6$ .—This base is precipitated from the solutions of its salts by hydrogen-sodium carbonate as a black powder. It is insoluble in hot water, hot alcohol, ether, and benzene, but dissolves easily and with deep brown colour in aqueous sodium carbonate or hydroxide (distinction from *cuprine*, Abstr., 1881, 314). Strong sulphuric and hydrochloric acids dissolve it with fine fuchsine-red colour, passing into blue-violet on addition of water. It dissolves in dilute mineral acid with blue-violet colour. The *hydrochloride*,  $C_{20}H_{18}N_2O_6, HCl$ , crystallises in needles having a coppery lustre. The base is not altered by heating with concentrated hydrochloric acid at  $100^\circ$ . The yield of cupronine from bromotarconine is about 10 per cent. Its mode of formation has not yet been distinctly made out.

*Nartine*,  $C_{20}H_{16}N_2O_6$ .—This base is obtained as a dihydrochloride by heating bromotarconine in sealed tubes with hydrochloric acid at  $120$ – $140^\circ$ . Its properties and reactions have already been sufficiently

described in this Journal (Abstr., 1881, 445). The author, in the present paper, changes its name to *nartic acid*, but the reason for this change is by no means obvious, as in all the compounds described, the body plays the part of a base.

The remainder of the paper is devoted to speculations concerning the molecular constitution of the bodies above described, and of cotarine. H. W.

**Action of Sodium on Lupinine.** By G. BAUMERT (*Ber.*, 15, 631—633).—Schulz has stated that by the action of sodium on lupinine two molecules of water are removed successively to form first a compound,  $C_{10}H_{19}NO$ , and secondly a compound,  $C_{10}H_{17}N$ . The author has repeated Schulz's experiments under various conditions, and finds that by the action of sodium on lupinine hydrogen is evolved; but he was unable to extract anything but lupinine from the fused product. V. H. V.

**Anhydrolupinine.** By G. BAUMERT (*Ber.*, 15, 634—636).—The author has put forward the view that by the action of concentrated hydrochloric acid on lupinine a molecule of water is removed with formation of an anhydrolupinine,  $C_{21}H_{40}N_2O_2 - OH_2 = C_{21}H_{38}N_2O$  (this vol., p. 229). In order to confirm this view, the author has studied the action of phosphoric anhydride on lupinine, and obtained, besides oxylupinine, a substance identical with this anhydrolupinine. The oxylupinine is separated by the sparing solubility of its platinochloride, and to the mother-liquor from the oxylupinine platinochloride crystals, alcohol is added which separates out the anhydrolupinine platinochloride in large quadratic tables. The free base was not isolated in the pure state; it rapidly turns red, and ultimately brown; undergoing decomposition at the same time. V. H. V.

**Discovery of Alkaloids from Proteid Animal Matter.** By A. GAUTIER (*Compt. rend.*, 94, 1119—1122).—A historical summary. C. H. B.

**Isocholanic Acid.** By P. LATSCHINOFF (*Ber.*, 15, 713—718; also *Journ. Russ. Chem. Soc.*, 1882, 170—175).—A continuation of the author's researches (Abstr., 1880, 722). The differences between the observations of Tappeiner and those of the author on the water of crystallisation of the barium salts and the action of nitric acid on cholanic acid, most probably arise from the fact that Tappeiner was dealing with a mixture of two isomerides.

The author has shown that by the oxidation of cholic acid with permanganate or chromic acid, two isomeric acids are produced, viz., cholanic acid and isocholanic acid. The iso-acid differs from its isomeride in the following particulars:—

(1.) The barium salt of the former is sparingly soluble in hot and cold water; the barium salt of the latter is easily soluble in cold water.

(2.) A solution of the barium salt of the former is not precipitated by carbonic acid, whilst a solution of the barium salt of the latter is easily precipitated.

(3.) The iso-acid forms a characteristic crystalline hydrogen potas-

sium salt, whilst the ordinary acid forms no such salts. The iso-acid differs also from its isomeride in its solubility in water, and in its specific rotatory power  $[\alpha]_D = +73.3$  ( $l = 300$   $p = 1.9327$  grams in 100 c.c.), while Tappeiner finds  $[\alpha]_D = 53$ , and Kutscheroff  $[\alpha]_D = 88$  for cholanolic acid. Isocholanolic acid forms delicate pearly scales (m. p.  $239^\circ$ ; cholanolic acid melts at  $285^\circ$ ).

The salts of isocholanolic acid have a similar composition to those of cholanolic acid, the neutral salts being represented by the formula  $C_{40}H_{51}MO_{12}$ , the hydrogen salts by the formula  $C_{20}H_{27}MO_6$ . The neutral potassium salt crystallises in fine hairy needles, stable in the air, and soluble in water and dilute alcohol. The hydrogen potassium salt is a crystalline sparingly soluble precipitate; its solubility increases with rise of temperature, and from hot saturated solutions it separates in delicate needles. The neutral barium salt,



is amorphous, sparingly soluble in cold water; it is altered even by exposure to air, to form probably a more stable combination of composition  $C_{20}H_{26}BaO_6$ . The lead salt is obtained as an amorphous precipitate by adding lead acetate solution to ammonium isocholanate. The silver salt is a thick amorphous precipitate, the copper salt a voluminous amorphous blue precipitate. Pure cholanolic acid is not oxidised by warming with nitric acid, but takes up a molecule of water and is converted into cholecamphoric acid; isocholanolic acid, however, is readily oxidised with production of an acid differing from cholecamphoric acid, but which could not be submitted to a minute investigation as the quantity of material was too small. V. H. V.

**Contributions to the Chemistry of Bile.** By G. HÜFNER (*J. pr. Chem.* [2], 25, 97—102).—The remarkable behaviour of the galls of Tübingen cattle with ether and hydrochloric acid has already been noticed by the author (*J. pr. Chem.* [2], 10, 267). It was thought that a study of the relative quantities of glycocholic and taurocholic acids in different samples of bile would explain why some crystallised at once on addition of ether and hydrochloric acid, and other kinds refused to do so. To this end, ten samples of bile were analysed, six of which gave a rapid crystallisation of glycocholic acid, one a weak one, and three none at all; it was found that the quantities of taurocholic and glycocholic acids respectively were as one to five in the samples from which the latter acid crystallised rapidly, and about equal in those where no crystallisation at all occurred. That this result had nothing to do with the question as to the absolute increase or decrease in quantity of each acid in the bile was shown by the fact that dilution in the one case did not put a stop to crystallisation, whilst in the other concentration did not induce it.

Again, experiments with mixtures of the pure salts of taurocholic and glycocholic acids showed that the relative proportion of the two acids present in solution together had very little, if any, effect on the crystallisation of the latter. Hence those biles in which there is no appearance of crystallisation of glycocholic acid on addition of ether and hydrochloric acid, must contain some other body, the presence of

which is possibly dependent on the nature of the animal's diet, and which prevents the crystallisation of glycocholic acid under those conditions.

J. K. C.

**Derivatives of Pyrocoll.** By G. L. CIAMICIAN and L. DANESI (*Gazzetta*, 12, 28—42).—Phosphorus pentachloride does not act on pyrocoll in the cold, but at  $220^{\circ}$  it yields *perchloropyrocoll*,  $C_{10}H_2N_2O_2$ , and in much smaller quantity another crystalline substance of the composition  $C_{10}Cl_{10}N_2O$ . These two are separated by treating the contents of the tubes with ether, in which the perchloropyrocoll is insoluble; the latter may be easily purified by washing the crystals with water to remove traces of phosphorus chloride, and then boiling it with glacial acetic acid to remove traces of the other chlorinated compound formed at the same time. It is only sparingly soluble in boiling acetic acid, and crystallises out on cooling in very thin plates of a pale-yellow colour, which melt with decomposition at  $320^{\circ}$ . The other compound,  $C_{10}Cl_{10}N_2O$ , produced at the same time as perchloropyrocoll, is obtained on evaporating the ethereal solution as a dark yellow crystalline mass; this is washed with cold alcohol to remove resinous matter, and then crystallised from boiling acetic acid in which it is readily soluble; the use of a little animal charcoal removes the colouring matter. It forms large iridescent prisms (m. p.  $195-197^{\circ}$ ) belonging to the trimetric system—

$$a : b : c = 2.20620 : 1 : 0.61196.$$

Forms observed, 100, 110, 101, 001; observed combinations, 100, 110, 101; and 100, 110, 001.

Perchloropyrocoll is not acted on by a cold solution of potassium hydroxide, but on boiling the mixture for some time the pyrocoll derivative is completely dissolved. On adding an acid to the cold solution, a bulky white crystalline precipitate of  *$\alpha$ -trichlorocarboxypyrillic acid*,  $C_5Cl_3H_2NO_2$ , is obtained; this crystallises readily from boiling water in tufts of long delicate silky needles containing 1 mol.  $H_2O$ , which, when heated to  $150^{\circ}$ , decompose violently without melting. It is very easily soluble in alcohol and in ether. The *ammonium* salt forms long colourless needles, soluble in water; the *barium* salt crystallises from alcohol in brilliant colourless scales.

When perchloropyrocoll is heated at  $250^{\circ}$  in closed tubes with phosphorus pentachloride for five hours and allowed to cool, the tubes contain besides phosphorus trichloride, large colourless crystals of a new substance, and a small quantity of unaltered perchloropyrocoll; the latter is in comparatively thick plates of a deep yellow colour. In order to isolate the new compound, the phosphorus trichloride is poured off, the residue is washed successively with water and alcohol, and is then treated with ether, which leaves the perchloropyrocoll undissolved. On allowing the ethereal solution to evaporate spontaneously, the new substance is deposited in large crystals, which may be purified by recrystallisation from acetic acid and ether; in order to remove the last traces of resinous matter, however, it is necessary to submit it to sublimation, when it is obtained in the form of long, very slender, colourless needles (m. p.  $146-147.5^{\circ}$ ) of the composition represented

by the formula  $C_5Cl_7NO$ . The vapour has an odour resembling that of camphor, and attacks the mucous membrane of the eyes and nose. The compound is sparingly soluble in alcohol or cold acetic acid, but easily in the boiling acid or in ether. The crystals obtained by spontaneous evaporation of the ethereal solution, or from its solution in boiling acetic acid, belong to the monoclinic system—

$$a : b : c = 0.73505 : 1 : 0.66191; \eta = + X : + Z = 102^\circ 10' 50''.$$

Forms observed, 110, 001, 111. Observed combinations, 110, 001, and 110, 001, and 111. Double refraction negative;  $\rho > v$ .

The chemical nature of this new compound is not yet made out, but from its behaviour with potassium hydroxide it would seem to have a constitution quite different from that of pyrocoll: when boiled with the alkaline solution, it evolves ammonia in abundance, and the potash salt of an extremely deliquescent acid is formed.

When pyrocoll is dissolved in cold fuming nitric acid, and then heated on the water-bath until nitrous vapours cease to be given off, it is converted into *dinitropyrocoll*,  $C_{10}H_4(NO_2)_2N_2O_2$ , which is thrown down as an orange-yellow precipitate on pouring the acid solution into water. It may be purified by crystallising it from boiling glacial acetic acid and the use of animal charcoal. It forms deep yellow plates, sparingly soluble in ether and alcohol even when boiling. When heated, it decomposes before fusing; and on platinum foil it burns with deflagration.

Dinitropyrocoll dissolves in cold potash solution with deep yellow colour; but if the solution is boiled the dinitro-derivative is decomposed with formation of the potassium salt of *mononitrocarbopyrollic acid*,  $C_6H_4N_2O_4$ . The acid may be isolated by acidifying the solution with sulphuric acid, and extracting with ether in the usual way. It crystallises in pale yellow silky microscopic needles (m. p.  $144$ – $146^\circ$ ) containing 1 mol.  $H_2O$ . It is soluble in water, alcohol, and ether. The *ammonium* salt forms large deep yellow scales, easily soluble in water; the *barium* salt crystallises in sparingly soluble orange-yellow scales.

C. E. G.

**Peptones and Alkaloids.** By C. TANRET (*Compt. rend.*, **94**, 1059).  
—A claim for priority over J. Béchamp.

C. H. B.

**Composition of Crystallised Albumin from Hemp and Castor-oil Seeds.** By H. RITTHAUSEN (*J. pr. Chem.* [2], **25**, 130–137).—Various preparations of albumin from hemp seed were made and analysed; their composition showed them to be identical with the crystallised albumin previously obtained by the author (*J. pr. Chem.* [2], **23**, 481). The following is the mean result of the analyses of crystallised albumin from hemp and ricinus seed:—

	Hemp seed.	Ricinus seed.
C.....	50.98	50.88
H .....	6.92	6.98
N.....	18.73	18.58
S.....	0.82	0.77
O.....	22.55	22.79

The samples of crystallised albumin therefore from the two sources show so close an agreement in composition that they may be assumed to be identical; this assumption is borne out by the resemblance in their crystalline form, and their behaviour with reagents. They dissolve in tolerably concentrated glycerol to an opalescent liquid, and are not reprecipitated therefrom by addition of water, being in fact soluble in the latter when quite free from adhering sodium chloride.

J. K. C.

**Crystallised Albumin from Pumpkin Seeds.** By H. RITTHAUSEN (*J. pr. Chem.* [2], **25**, 137—141).—Careful analyses of this body, whether burnt with copper oxide or lead chromate, always gave a higher percentage of carbon than in the case of albumin from hemp seed and castor-oil seed, but in no case were Grüber's numbers obtained, the latter finding 1·8 per cent. carbon and 0·2 per cent. hydrogen more than Ritthausen, whose analyses agree very well with those of Barbieri referring to amorphous albumin from pumpkin seeds.

J. K. C.

**Insoluble Modification of Pepsin.** By A. GAUTIER (*Compt. rend.*, **94**, 1192—1195).—The insoluble granules obtained from pepsin (this vol., p. 752) are gradually but slowly converted into the soluble modification in presence of pure water. This affords proof of Béchamp's supposition (this vol., p. 752) that pepsin is a product of these gastric microzymas, as he terms the insoluble granules. The author is, however, unable to agree with Béchamp that these granules are living organisms which have the power of secreting pepsin. He regards them as a purely chemical ferment, without organisation and without life, and bases this conclusion on the following facts. The granules show no signs of organised structure under the highest magnifying power; they do not propagate even under most favourable conditions; they digest albuminoids in presence of poisons which completely check the activity of organised ferments, especially such as are of the nature of vibrioles, and they act only in presence of free acids, whereas bacteria and their germs require a neutral or alkaline medium.

The insoluble granules can be easily obtained from the mucous membrane of a pig's stomach from which all mucus has been removed. Thus obtained their properties agree with those of the *gastric microzymas* of Béchamp.

C. H. B.

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## Physiological Chemistry.

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**Digestion in the Stomach.** By A. KIETZ (*Chem. Centr.*, 1882, 46).—In normal gastric juice and during the first hour of digestion, lactic acid is absent. The acid of gastric juice is hydrochloric, which is free to a certain extent. Colour reactions are useless for distinguishing lactic and hydrochloric acids, as peptone, &c., behave in a similar way. Velder's statement that carcinoma of the stomach is unac-

accompanied by the presence of free acid, whereas free acid is present with chronic catarrh, is corroborated. E. W. P.

**Formation of Fat in Animals.** By B. SCHULZE (*Bied. Centr.*, 1882, 239—244).—Geese were fed with a mixture of rye, bran, and starch, so arranged that for each pair of birds the nutrient ratio should be 1 : 5·1, 1 : 7·4, and 1 : 9·6; originally there were eight birds, all previously being fed with a mixture whose nutrient ratio was 1 : 5, but before the experimental mixture was given, two birds were killed so as to determine approximately the amount of fat, bone, &c., present in the set. At the end of the experiment each bird had received the following food constituents in grams:—

	N. R. 1 : 5·1.		N. R. 1 : 7·4.		N. R. 1 : 9·6.	
Albuminous N ..	319·38	318·0	237·49	237·49	188·35	188·35
Fat .....	544·50	542·2	404·90	404·90	321·10	321·10
Starch .....	12095·50	12043·3	12884·60	12884·60	13358·20	13358·20

It was taken for granted that the amides would be completely absorbed, therefore only the other undigested constituents were looked for in the excrement.

*Amount of Food digested in grams.*

	N. R. 1 : 5·1.		N. R. 1 : 7·4.		N. R. 1 : 9·6.	
Albuminous N ..	112·30	111·79	83·75	83·75	55·61	55·61
Asparagin .....	56·28	56·04	41·85	41·85	33·19	33·19
Fat .....	221·80	220·78	205·00	205·50	202·50	202·50

Employing then Voit's (46·7 per 100 albumin) and Henneberg's factors (100 asparagin for 17·8 fat), it is calculated that each bird had formed fat without the aid of carbohydrates to the following amounts in grams: 604·89, 602·25, 490·67, 490·67, 396·72, 396·72 respectively. The birds having been killed, were found to have put on the following amounts of fat: 387·1, 539·3, 515·1, 612·2, 491·9, 471·0, in addition to what they had previous to the commencement of the experiment, the quantity then present being supposed to be approximately the same as possessed by the two geese killed at the beginning. As then the fat was in excess of that which could be produced by the conversion of the nitrogenous matter to the amount of about 20 per cent., the conclusion is drawn that when the nutrient ratio is wider than 1 : 5 the carbohydrates play a distinct part in the formation of fat in the carnivora and herbivora. E. W. P.

**Formation of Bile.** By SPIRO (*Bied. Centr.*, 1882, 244).—The percentage of sulphur in bile varies between 1·88 and 3·41, but the



variation bears no relation to the kind and quantity of food, and the amount seems slightly to decrease with a change of food, increasing later on. Of nitrogen, 7.23—10.66 appears, but to what compound this large amount of nitrogen belongs is unknown.

Total solids vary from 4.09—7.88 per cent.; watery food does not affect this. Whilst the bile is but slightly affected by albuminous food, the sulphur increases in the urine. E. W. P.

**Physiological Activity of Superoxygenated Molecules, especially those of Quinine Iodate and Bromate.** By C. A. CAMERON (*Chem. News*, 45, 227).—The term "superoxidised" is applied to those molecules which contain a larger number of oxygen-atoms than are requisite to saturate the other atoms present, but at the same time these oxygen-atoms are unsaturated, therefore the compound is unstable. As examples of such bodies there are bromic and iodic acids, whose alkaline salts are less stable than the iodide or bromide of potassium, &c. It was thought that such unstable or superoxidised bodies would be more physiologically active than the simpler compounds; such a supposition appears to be correct, and quinine iodate and bromate are now largely prescribed in place of other compounds of quinine. The iodate is prepared by dissolving hydrated quinine in iodic acid, and it occurs as fine white pearly-lustred crystals,  $C_{20}H_{24}N_2O_5HIO_3$ , which are not altered at  $60^\circ$ . Quinine iodate is soluble in alcohol, hydrochloric acid, and in 700 parts of cold water; it is but slightly altered by strong sulphuric acid, or by heating at  $100^\circ$ . The bromate may be prepared either by directly neutralising quinine with bromic acid, or by decomposing the sulphate with barium bromate, when it forms asbestos-like masses, which are not decomposed at the heat of the water-bath; they also dissolve in alcohol, hydrochloric acid, and in 250 parts of water. Strong sulphuric acid decomposes the bromate with detonation. Continued boiling of the solution in water causes the formation of a blue coloration, which is bleached by nitric acid. Shortly after administration of quinine iodate, iodic and hydriodic acids appear in the urine; later on, the quinine makes its appearance.

E. W. P.

**Potassium Permanganate as an Antidote to the Poison of Bothrops.** By COUTY (*Compt. rend.*, 94, 1198—1201).—As the result of a number of experiments on dogs, the author concludes (1) that the recommendation of potassium permanganate as a remedy in cases of bites by venomous serpents is not based on sufficient experimental evidence; (2) that it is no antidote to the poison of *Bothrops*, when the poison has entered the blood or the different anatomical elements of the tissues.

C. H. B.

**Relation between the Isomorphism, Atomic Weights, and Toxic Effects of Metallic Salts.** By J. BLAKE (*Compt. rend.*, 94, 1055—1057).—Richet (*Compt. rend.*, 1881) has compared the toxic effects of different metallic salts by dissolving them in water and placing fish in the solutions, and concludes that there is no relation between the poisonous properties and chemical functions of the metals. It is, however, well known that the effect produced by many poisons

when brought in contact with the mucous membrane is very different from that which they exert when introduced directly into the blood. Moreover, in the cases under consideration, the effects would be modified by the differences between the coefficients of diffusion of the different salts, by the rapidity with which they are eliminated from the system, and by differences in their local action on the tissues. The author has made many experiments by introducing different metallic salts *directly into the blood* of living animals, and finds that the physiological action of a salt depends on the base, and is not materially affected by the nature of the acid. Further, this action is intimately connected with the isomorphic relations of the salts, substances in the same isomorphous group producing similar effects. In the same group, the toxic effect is greater the higher the atomic weight of the metal. Amongst thirty metals, the only exception to the last law is in the case of potassium and sodium. These metals have not anything like the toxic effect assigned to them by Richet. His results were affected by the fact that the rate of diffusion of potassium salts is much greater than that of any others which he used, and they also enter the blood through the branchial membrane much more easily. The results obtained by the author with metallic salts are strictly analogous to those obtained by Dugardin with homologous series of alcohols.

C. H. B.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Peptone-forming Ferment in Plants.** By C. KRAUCH (*Landw. Versuchs.-Stat.*, **27**, 383—386).—Schulze and Barbieri (this vol., 318), and Gorup-Besanez found a peptone-forming ferment in many seeds and sprouts. Krauch has followed exactly Gorup-Besanez's process, and although he obtained the same results (*Ber.*, **7**, 1478), comes to the conclusion that the substance formed is no ferment. His reason is that the biuret reaction is obtained with the original substance, even before the "ferment" comes in contact with any albuminoid matter.  
E. W. P.

**Influence of Space on the Growth of Plants.** By E. WOLLNY (*Bied. Centr.*, 1882, 254—261).—III. Drilling-in the seed produces a heavier crop of grain and straw than broadcast sowing, whether the seed sown be in equal or unequal quantities. The fertility of the plants from drilled seed is the highest, and the quality also, as larger and heavier grains are formed. The reasons are probably that by drilling the seed is laid more evenly and at the same depth in the soil, and also it has been observed that the soil in the drills had a higher temperature than when the broadcast method was employed; a saving of 20—40 per cent. of seed-corn is also effected. Dibbling, when like quantities of seed are used is better than drilling, and even when less seed is used for dibbling the yield is higher than when a

larger quantity of seed is drilled. However, for grasses, clovers, &c., which are to be used green, thin broadcast sowing is best for the plants; being close together and more shaded they remain tender and more digestible. A special set of experiments are also described, in which the distance of the drills from one another was equal, but the amount of seed not so; also when drills were uneven in distance but the seed equal (per unit of surface unequal); and again when the drills were unequal but the seed per unit of surface equal. In the first case, the maximum yield occurs when a definite distance is attained; when that increases or diminishes the yield is affected, and the quantity and fertility of the plants are better the fewer the plants in a row. In the second case, there was also a definite point at which the maximum yield was produced, and the wider apart the yield so much the better the crop. In the last case, the yield the smaller amount of seed used produced the best crop.

E. W. P.

**Influence of Certain Substances on Plant Cells and Ferments.** By W. DETMER (*Chem. Centr.*, 1882, 46).—The question whether certain processes in plants are due to fermentation or to dissociation has to be answered by allowing like substances, under like conditions, to act upon living cells and ferments. If the first theory be correct, then the results of the reactions will be identical. Sprouts of barley, wheat, and peas were allowed to remain in contact with certain solutions, and these were compared with a mixture of malt extract and starch added to the same solutions. The results were, neither the vitality of the sprouts nor the action of the ferments were destroyed by grape-sugar; salicylic acid and copper sulphate destroyed both; the vitality of the sprouts was destroyed, but not that of the ferment, by phenol, quinine hydrochloride, carraway oil, and chloroform; phosphoric and citric acids destroyed the ferment, but not the sprouts. From these results, it is inferred that the change in plants is not due to fermentation.

E. W. P.

**Origin of Saccharine Substances in Plants.** By A. PERREY (*Compt. rend.*, 94, 1124—1125).—The author has estimated the amount of sugar in different parts of the kidney-bean plant at different stages of growth, with the following results. The numbers give the percentages of sugar in the dried plant:—

	Glucose.		Saccharose.	
	Leaves.	Stalks.	Leaves.	Stalks.
June .....	1.6	2.5	5.6	9.0
„ 29th ....	—	—	5.6	3.8
July 7th .....	—	3.6	4.1	5.1
„ 15th .....	—	2.0	0.8	5.0
„ 29th .....	—	1.1	2.2	6.4
August 13th ..	—	0.9	traces	3.0
„ 26th ..	1.0	1.4	2.4	2.8
September 11th	1.2	2.3	4.2	3.0
„ 23rd	1.4	1.5	4.2	2.7

From June 29th to July 29th, glucose does not exist in the leaves, but it appears in the stalks on July 7th, and is present on July 29th. It would therefore appear that glucose is not a direct product of the elaboration of chlorophyll. Saccharose, on the other hand, is present in the leaves from June 29th to July 29th, and the simultaneous absence of glucose would appear to show that saccharose is a direct product of the elaboration of the green cellules, and that its formation does not depend on the decomposition of starch expressed by the equation  $3C_6H_{10}O_6 + H_2O = 2C_6H_{10}O_5 + C_6H_{12}O_6$ . Glucose was not found unaccompanied by saccharose in any part of the kidney-bean, oat, or maize plant, from which it would appear that the former is a product of the hydration of the latter. The small quantity of starch in the chlorophyll cells is probably produced by a secondary reaction between the saccharose and glucose, which unite in the proportion of equal molecules: this reaction is secondary in the leaf, but becomes the principal reaction in the grain. Frequently the molecules of glucose are more numerous than those of saccharose, and it is possible that this glucose which does not form starch, plays an important part in the formation of complex glucosides or of nitrogenised bodies.

Under the term glucose are included those sugars which reduce Fehling's solution directly, and under the term saccharose those which reduce it after inversion.

C. H. B.

**Reducing Action of Living Protoplasm.** By O. LOEW and T. BOKORNY (*Ber.*, 15, 695—698).—Reinke (*Ber.*, 15, 107) has observed that the presence of aldehyde substances in plants, as detected by the authors' reaction with silver nitrate, is only a property of the protoplasm of the chlorophyll. But the authors show that cotyledons of the helianthus, the hairs of plants, the cells of fruits, and the sap of the pine and the oak, give an aldehydic reaction, as well as many of the higher fungi, the algæ, and many infusoria. It is further shown that many objects which under ordinary conditions show this reaction, yet may give a negative result, as spirogyra in the act of copulation, or protoplasm in which is embedded a large quantity of lecithin. With animal protoplasm, no result could be obtained, owing to its death before the reaction could set in, or to the presence of chlorides and nitrates. However, it is well known that after application of silver nitrate, metallic silver appears in various parts of the body, especially in the corium, which is doubtless dependent on the aldehydic reaction of the living protoplasm. It is also noticed that while the cotyledons of the helianthus reduce silver nitrate, yet the cotyledons of peas do not show this reaction; the difference may be due to the presence of lecithin in the latter. A similar difference is observable with osmic acid, which the tissues of the helianthus reduce to metallic osmium, while the tissues of the pea reduce it only to osmic oxide by the amido-acids which arise from the decomposition of the albumin.

V. H. V.

**Influence of Light on the Germination of Grass-seeds.** By F. NOBBE (*Landw. Versuchs.-Stat.*, 27, 346—355).—According to Wagner, the seeds of *Poa pratensis* germinate more rapidly in the light

than in the dark. This statement being in direct opposition to those of Ingenhous, Fleischer, and others, it was determined to investigate the matter as fully as possible, and for that purpose arrangements were made that germination should take place in the light and in the dark in (1) moist sand; (2) in thick moist filter-paper; (3) in garden mould. Of the seeds of *Poa pratensis*, 65·5 per cent. germinated during July in the dark, and 55·17 in the light; and in August, of a fresh sample 65·5 and 46·25 per cent. germinated. Here we find a retarding influence exerted by light. Moreover, not only is the total percentage of seeds germinated in light lower, but the commencement of the change is later. In a second set of experiments with the same seeds, sown in January and in August, the percentages were, in January, 67 in the dark, and 61·8 in the light; whilst for August, we find 70·17 and 58·5 per cent. respectively. Here again the retarding influence of light manifests itself, the depression being greater in July than in January, evidently by reason of the increase in the duration of the light. With *Dactylis glomerata*, however, there seems to have been no difference, the figures being practically the same. Samples of *Phleum pratense* germinated to the extent of 91 per cent. in the dark, and 89·5 in the light, but although the end results are very similar, yet examination of the daily progress shows that the light retarded the commencement of germination, and caused it to be very irregular. A further set of experiments in direct sunlight was instituted with maize, and then it was found that of these seeds 67 per cent. germinated in the dark, after 11 days, and only 8 per cent. in the light; after 18 days longer a few more of the exposed seeds germinated, but they soon died. The results of the experiments show that light is prejudicial to the germination of seeds. The author has received a pamphlet by Stebler, in which it is stated that light aids the germination of seeds, especially the grasses, and that those seeds in the dark will scarcely grow at all. As this statement was directly opposed to his own results, the author believes that there must be some fault in the method of experimenting.

E. W. P.

**Part played by Fat during the Germination of Seeds.** By M. A. LADUREAU (*Chem. Centr.*, 1882, 44—46).—Fats, by their decomposition, evolve heat, which is necessary for germination, at the same time producing glycerol and glucose. The germination of seeds requires a period of time depending on the thickness and hardness of their skins, which, if hard, prevent the access of moisture and air to the interior, and consequently the decomposition of the fat is retarded. The oil is always acid in those seeds which have lost their germinating power, whereas it is neutral in healthy seeds.

E. W. P.

**Analysis of Wild Vetch.** By P. BAESSLER (*Landw. Versuchs-Stat.*, 27, 415—416).—The analysis of the dried plants of *Vicia cracca*, grown on unmanured Greywacke soil in Westphalia, is as follows:—H<sub>2</sub>O, 15·6; ash, 5·76; organic matter, 78·64. Dried at 100°: ash, 6·83; albumin, 27·37; fibre, 19·99; fat, 1·43; extracts, 44·38. The ash contains 37·02 per cent. K<sub>2</sub>O and 10·28 of P<sub>2</sub>O<sub>5</sub>.

E. W. P.

**Cucurbitaceæ of Uruguay.** By SACC (*Compt. rend.*, **94**, 1126—1128).—The author has examined only those species which are sold in the markets of Monte Video. They constitute an important article of national food, and are regarded as highly nutritious. The pulp was found to have the following composition:—

	1.	2.	3.	4.	5.	6.
Gum .....	0.44	0.58	0.66	0.58	0.36	1.20
Sugar .....	2.52	3.86	5.10	4.86	1.50	3.80
Starch .....	13.73	1.24	2.70	7.18	0.99	1.96
Albumin.....	—	0.02	0.20	0.09	traces	—
Fibrin .....	0.47	0.08	0.01	0.01	0.04	0.02
Lignose .....	0.22	0.72	0.81	0.78	0.74	1.02
Ash.....	0.81	1.38	0.50	0.90	0.48	1.00
Water .....	81.81	92.12	90.02	85.60	95.89	91.00

100.00 100.00 100.00 100.00 100.00 100.00

	7.	8.	9.	10.	11.
Gum .....	0.44	0.64	0.42	0.08	0.46
Sugar .....	1.02	4.88	3.71	4.86	4.06
Starch.....	0.97	3.40	—	0.04	—
Albumin.....	—	traces	—	—	—
Fibrin.....	0.34	0.36	0.01	—	0.02
Lignose .....	0.88	0.62	0.47	0.94	0.76
Ash.....	0.90	0.70	1.00	0.80	0.60
Water.....	95.45	89.40	94.39	93.28	94.10

100.00 100.00 100.00 100.00 100.00

(1.) The best variety, *Bubango*, deep green; pericarp 37, orange pulp 49, large white seeds 4 = 100. (2.) *Criollo*, spherical; very thick and hard, wrinkled, grey pericarp 36, orange pulp 52, large white seeds 12 = 100. (3.) *d'Angola*, pericarp 48, pulp 34, large white seeds (which contain 23.2 per cent. of a fatty oil), 18 = 100. (4.) *d'Andai*, pericarp 60, pulp 36, seeds 4 = 100. (5.) *d'Irunco*, pericarp 48, pulp 43, seeds 9 = 100. (6.) *Turban*, a variety of *d'Irunco*, consisting of two fruits fitting one into the other, the lower orange, the upper citron-yellow; pericarp 68, pulp 24, seeds 8 = 100. (7.) *Pâtisson* or *Bonnet de Curé*, pericarp 59, pulp 30, seeds 11 = 100. (8.) *Melon*, pericarp 28, pulp 62, seeds 10 = 100. The seeds have a nankeen colour, are very thick and perfectly smooth, and contain 11 per cent. of a fatty oil. (9.) *Melon*, common; pericarp 63, pulp 35, seeds 2 = 100. (10.) *Pastèque*, pericarp 56, pulp 41, seeds 3 = 100. (11.) *Cidro*, pericarp 49, pulp 46, seeds 5 = 100.

The *Bryonæ*, often regarded as wild potatoes, but poisonous, have the composition:—

Pectic acid .....	0.33
Lignose .....	9.65
Inulin .....	5.32
Grape-sugar .....	4.86
Water and loss .....	79.84

100.00

C. H. B.

**Occurrence of Ammonia in Plants.** By H. PELLET (*Chem. Centr.*, 1882, 41—43).—The occurrence of ammonia in plants is more general than is usually supposed, as it is, for the most part, found only in roots. It occurs, however, in many other plants and seeds as magnesium ammonium phosphate. The dried leaves of sugar-beet contain 0.1555 per cent., the seeds about 0.2 per cent., the dried root itself 0.196—0.147 per cent., in grain 0.16, and in mixed meal 0.188 per cent. It is therefore clear that when much sugar is manufactured, a very large loss of valuable material occurs. In seeds, the ammonia is also in combination with sodium or potassium phosphate. The presence of these compounds accounts for the small amount of carbonates found in the ash of grain, for by the heat the ammonia is volatilised, and the liberated phosphoric acid replaces the carbonic anhydride.

E. W. P.

**Contributions to the Knowledge of the Nitrogenous Constituents of Potatoes.** By E. SCHULTZE and E. EUGSTER (*Landw. Versuchs.-Stat.*, 27, 357—373).—In former publications, it has been shown that the nitrogenous constituents of roots and tubers consist of albuminoids and amido-compounds; this paper contains an account of the processes employed for the quantitative determination of these compounds in four varieties of potatoes, viz., Bodensprenger, Rose, König der Frühen, and Biscuit. In the earlier experiments, no peptones were discovered in the juice of these potatoes, because animal charcoal, which absorbs peptones, was employed to decolorise the juice; but in the present series the expressed juice, being first coagulated by heat and acetic acid, and the coagulum removed, was decomposed by lead acetate (avoiding an excess); then the filtrate was acidified with sulphuric acid and precipitated with phospho-tungstic acid. The precipitate after being washed with acidulated water, was decomposed by baryta-water: the yellowish filtrate containing the peptones was treated with carbonic anhydride, which precipitated the colouring matter along with the barium carbonate. It was somewhat difficult to estimate the quantity of peptone in solution, but by employing a standard solution of fibrin-peptone, and using the biuret reaction (dilute copper solution), 0.016—0.021 gram per 100 c.c. juice was estimated. Again, the peptones were precipitated by tannic acid after precipitation of the albumin by lead, when 0.03—0.04 per cent. was found. The appearance of the phospho-tungstic precipitate, as well as the variation in the two results, led the authors to suppose that this acid carried down other matters besides peptones; they therefore employed the method of fractional precipitation with the result that the first precipitate was flocculent, the final precipitate pulverulent, and this form contained no peptones, but another nitrogenous body, probably allied to xanthine, shown to be present in plants by Solomon, Schützenberger, and others. As a further proof that peptone is not the only compound precipitated from the juice by phospho-tungstic acid, it was found that the quantities of nitrogen removed from like samples of juice by this acid and by tannic acid were not the same, the former acid removing the largest amount. The four kinds of potatoes under consideration appear to contain varying quantities of asparagine. Rose, though rich in non-albuminous nitrogen, is, however, poor in asparagine. The solutions prepared by



diffusion (the process is fully described and a sketch is given of the apparatus employed) contained, besides asparagine, also tyrosine and inorganic salts; of the latter, quantities varying from 6—18·9 per cent. of the crude crystallised mass obtained by evaporation of the solution. The amount of asparagine was estimated by crystallisation and by the ammonia produced by boiling with sulphuric acid (Sachsse); it was found that the last was the only accurate method. The amido-acids (leucine and tyrosine) were separated by alcohol from the dried potato (Abstr., 1880, 342), but a less troublesome process was to allow the tyrosine to crystallise before or with asparagine from the concentrated diffusate, when, in the case of Rose, 1 litre juice yielded 0·05 gram. Leucine was obtained from this mother-liquor by adding alcohol to it and evaporating. The whole of the nitrogen in the form of asparagine, leucine, &c., can be determined in the filtrate from the phospho-tungstic acid precipitate. The following table shows percentage of albuminous (including peptones) and non-albuminous matter present, as estimated by the processes described:—

	Albumin.	Non-albu- minous.	Albumin in whole potato.
Bodensprenger .....	65·4	34·6	1·19
Rose .....	43·9	56·1	0·65
König der Frühen.....	48·4	51·6	0·87
Biscuit.....	57·5	42·2	1·06

These figures correspond well with those obtained in the previous year.

In an additional note it is stated that before the nitrogen can be correctly estimated by Sachsse-Kormann's process, all the ammonia must be removed by evaporation with magnesia before boiling the juice with sulphuric acid.

E. W. P.

**Analysis of a Vegetable Fat.** By F. REINITZER (*Monatsh. Chem.*, 3, 266—271).—This fat, from an unknown locality, has the colour, consistence and odour of cacao-butter, and a faint acid reaction. In the crude state, it is mixed with a large quantity of vegetable fragments—wood, bark, and seeds—which were found by microscopic examination to belong to a plant of the Anacardiaceous order. The fat, purified from these by means of a steam-filter, melts at 41°. By saponification; decomposition of the resulting soap with hydrochloric acid; separation of the oily from the solid fatty acids, by crystallising the precipitated mass from boiling alcohol; pressing the crystalline mass between cloths; twice recrystallising the press-residue from alcohol; and subjecting both the crystallised product thus obtained, and the alcoholic filtrates, to fractional precipitation with barium salts according to Heintz's method, it was found that the solid portion consisted wholly of stearic, and the oily portion of oleic acid; and the relative quantities of these acids showed that the fat was a mixture of 57·88 per cent. tristearin and 42·12 triolein.

In connection with the course of analysis above indicated, the author observes that barium oleate must be dried in a vacuum over sulphuric acid, as when heated at 100° under ordinary pressure it con-

tinually loses oleic acid and is converted into a basic salt. Barium stearate, on the other hand, may be dried at  $100^{\circ}$  without alteration. Further, in preparing the normal ammonium salts of fatty and oily acids, it is necessary to keep an excess of ammonia in the solution, as otherwise the residue left on evaporation will consist, not of a normal but of an acid salt.

H. W.

### Deposit of Calcium Carbonate in Dicotyledonous Trees.

By H. MILOSCH (*Chem. Centr.*, 1882, 43).—Calcium carbonate may be found deposited in crystals in the cells of woody plants far oftener than is generally supposed, and the cells are often so completely filled that the salt assumes the form of the cell.

E. W. P.

### Analysis of the Ash of the Various Parts of *Aster Amellus*.

By C. COUNCLER (*Landw. Versuchs.-Stat.*, 27, 375—382).—The principal parts of the *Aster amellus*, a lime plant, were separately estimated, with the following results:—

	Roots.	Stems.	Leaves.	Blossom.
Air-dried substance . . . .	17.77 p. c.	37.04 p. c.	28.66 p. c.	16.53 p. c.
Ash . . . . .	6.39 „	3.87 „	10.08 „	6.51 „

#### Percentage Composition of Ash.

SiO <sub>2</sub> . . . . .	9.71	1.03	4.59	—
SO <sub>3</sub> . . . . .	11.49	7.88	7.44	9.70
P <sub>2</sub> O <sub>5</sub> . . . . .	3.11	5.55	3.72	10.66
Fe <sub>2</sub> O <sub>3</sub> . . . . .	6.42	0.68	0.59	0.63
Mn <sub>2</sub> O <sub>4</sub> . . . . .	0.81	1.29	1.11	0.99
MgO . . . . .	4.28	3.80	5.58	6.14
CaO . . . . .	33.73	32.29	34.48	23.96
K <sub>2</sub> O . . . . .	28.98	44.16	41.82	46.66
Na <sub>2</sub> O . . . . .	1.46	3.32	0.67	1.26
	99.99	100.00	100.00	100.00

Although SO<sub>3</sub> is entered in the above analysis, the figure is incorrect, owing to the process of incineration. It, as well as chlorine, was determined in the moist way on the original materials. Of these were found in the roots 0.212 per cent. Cl, 0.334 per cent. SO<sub>3</sub>; in the stems 0.359 Cl, 0.0426 SO<sub>3</sub>; in the leaves 0.637 Cl, 0.634 SO<sub>3</sub>; and in the blossom 0.851 Cl, 0.572 SO<sub>3</sub>. Examination of the analytical figures shows that the large amount of potash present increases towards the blossom, and that it forms about one-third of the whole ash; the blossom contains no silica, whereas phosphoric acid forms a large fraction; compared with the ash of *Aster Tripolium* (*Botan. Centr.*, 7), the small amount of soda present in *A. amellus* is remarkable, as also the high percentage of iron and manganese. Chlorine and phosphoric acid increase in the upper portions of the plant, and lime is at its maximum in the leaves.

E. W. P.

**Researches on Plant Parasites and Plant Diseases.** By J. KÜHN and others (*Bied. Centr.*, 1882, 270—272).—Kühn reports the discovery of a parasite in lucerne and red clover, which has been called *Tylenchus Havensteinii*; it measures 1.43 m.  $\times$  0.0301 mm., and is somewhat longer and more slender than *T. devastatrix* which lives on rye. J. Brummer finds that the cause of the premature blanching of rye-straw is due to the larva of *Cephus pygmaeus* and *C. troglodytes*, as well as to the caterpillar of the rye-moth and *Thrips cerealium*, also the damage to the roots is occasioned by the wire-worm and cockchafer. Oehmichen ascribes clover sickness to the action of a trichina-like parasite, which fixes itself in the pith; this worm, also, is dangerous to rye, oats, and buckwheat; strong kainite manuring is recommended. E. W. P.

**Contributions to the Phylloxera Question.** By HENNEGUY and others (*Bied. Centr.*, 1882, 268—270).—Henneguy obtains good results by the use of carbon bisulphide and potassium thiocarbonate; the effect of the first substance on the vines is to render the bunches shorter and reduces the number of berries, although the bunches remain strong and the leaves green. J. Pastre reports that to prevent injury to the vines by the use of carbon bisulphide, the soil must not be too moist; that it is no use to treat the vines if the disease has made much progress; that the treatment must be done in mild winter weather; that the points of application should be increased and the dose diminished if the vines are in heavy soil and they have been long attacked; and they must be well manured, with an addition of potash salt to the stable dung. Avignon recommends tar as a cure. U. Gayon has made unsuccessful researches for parasites in the phylloxera. F. v. Thümen finds bromine, as recommended by Youillond-Dépret, to be too costly and dangerous. P. Mouillefert thinks that all vines, however much diseased, can be regenerated by the use of thiocarbonate. E. W. P.

**Some of the Conditions Influencing the Quality of Barley for Malting and Feeding Purposes.** By H. TANNER (*Journal of the Bath and West of England Society*, 1881, 54—63).—The quality of barley for malting purposes depends on the amount of starch present, and this is reduced if the land is in high condition, and albuminoids appear in its place, so that the grain is more adapted for feeding purposes. Barley after roots is not good for malting, but if it follows wheat, then its malting quality is improved. The experiments referred to show that nitrate of soda is injurious to barley in this respect, and that ammonia produces a large amount of unmaturred (non-albuminous) nitrogenous matter; so that it is evident that it is not the nitrogenous manure which is injurious, but rather the form in which it is presented. All recent animal manures are objectionable. Nitrate of soda seems to have produced an over-growth of weak straw. E. W. P.

**Cultivation of Osiers.** By KRAHE (*Bied. Centr.*, 1882, 251—254).—Of the varieties of willows grown, *Salix amygdalina* appears to be the most profitable. It grows the most abundantly on any soil, yields

the greatest number of wands, and the most wood. The distance apart at which the plants should be placed should be 40 : 10 cm.

E. W. P.

**Absorptive Capacity of Humous Matter.** By A. KÖNIG (*Bied. Centr.*, 1882, 228—237).—The final results of the investigation on the absorptive capacity of several kinds of soils rich in humus for ammonia, potash, and carbonate, chloride, nitrate, sulphate, and phosphate of ammonia, may be summed up in the following sentences:—Absorption is both physical and chemical; in the first case no alteration takes place; but in the second decomposition occurs between the added salt and the minerals in the soil; alkaline solutions are retained mechanically by humus, the amount increasing as the quantity of mineral matter decreases; potash and ammonia as neutral salts are retained by interchange, the amount rising with increase of mineral matter; chlorine, sulphuric and nitric acids are not retained, and phosphoric acid only if minerals are present which will form an insoluble phosphate. Moorland soils absorb water from solutions, rendering them more concentrated.

E. W. P.

**Manuring Vines.** By A. STUTZER (*Bied. Centr.*, 1882, 238).—As the preparation of farmyard manure in wine-growing districts is costly, it was determined to manure each vine with 6—7 grams soluble phosphoric acid, 5—6 grams potash, and  $2\frac{1}{2}$ —3 grams nitrogen. The results were in favour of the artificial manure, which raised the yield 39 per cent. The addition of nitrogen can be recommended only for Burgundy and not for white grapes.

E. W. P.

**The Rain and Drainage Waters collected at Rothamsted.** (Parts I, II, and III.) By J. B. LAWES, J. H. GILBERT, and R. WARINGTON (*Jour. Roy. Agri. Soc.*, 1881, 241—279, 311—350; 1882, 1—71).

**I. Rain-water.**—Rain has been collected since 1853 in a gauge of the area of  $\frac{1}{10000}$ th of an acre; the average rainfall, 1853—80, has been 28.30 inches. Ammonia was determined during 15 months, 1853—4, in mixed samples representing the rainfall of each month, the method being fractional distillation in glass vessels, and titration of the distillate; the mean result was 0.74 nitrogen as ammonia per million of water. Ammonia was determined by a similar method by Way, during 1855 and 1856; the mean amounts of nitrogen found as ammonia in the annual rainfall were respectively 0.88 and 1.18 per million. The mean amount of nitrogen as nitric acid was 0.12 per million in both years. The ammonia determinations during these three years showed an average of 6.10 lbs. of nitrogen supplied in rain per acre per annum; the nitrogen supplied as nitric acid during two years averaged 0.74 lb.; the total nitrogen was thus 6.84 lbs. Frankland analysed samples of single rainfalls during 1869—70; 69 samples gave a mean of 0.37 nitrogen as ammonia, 0.14 nitrogen as nitric acid, and 0.19 organic nitrogen, per million of water. The quantity of ammonia found by Frankland, using the Nessler method, was thus much smaller than that shown by the earlier titration method. Recent determinations at Rothamsted by the Nessler method confirm Frankland's results. The total amount

of nitrogen supplied by rain in the open country is thus probably only 4—5 lbs. per acre per annum; this is exclusive of condensation by the soil. The mean of 22 series of determinations, each extending over one year, made by various methods at nine Continental stations (some near towns), gives 10.23 lbs. of nitrogen per acre, as supplied by the annual rainfall. The mean quantities of the other constituents of rain found by Frankland were: total solid matter, 33.1; organic carbon, 0.90; chlorine, 3.1; total hardness, 4.7 per million. Rain collected on a washed gauge was purer than the ordinary collections.

Rain-water varies extremely in composition, all constituents being greater in small deposits than in large. Comparing together rainfalls of similar amounts, it appears that in summer rain is richer in total solid matter, organic carbon, ammonia, and nitric acid, whilst in winter it is richer in organic nitrogen and chlorine. The mean proportion of organic nitrogen to carbon is 1 : 4.8; in summer, when fresh vegetable matter is abundant, the proportion of carbon being more than twice as great as in winter.

The chlorine in mixed monthly samples of the rain has been determined since June, 1877; the mean of the first 43 months is 1.75 per million, or 13.42 lbs. per acre per annum. At Cirencester during 10 years the average has been 4.28 per million, or 32.5 lbs. per acre.

II. *Drainage from Uncropped, Unmanured Soil.*—The proportion of the rainfall percolating through the soil has been ascertained at Rothamsted by three drain-gauges, each of the area of  $\frac{1}{1000}$ th of an acre, containing a heavy loam, with clay subsoil, 20, 40 and 60 inches in depth. The soil is in its natural state of consolidation, having been built round and undermined without disturbance. It is kept free from vegetation, and unmanured. During 10 years, 1870—1880, with an average annual rainfall of 31.036 inches, the mean drainage in winter (October—March) has been 9.696 inches; in summer (April—September), 4.393 inches; in the whole year, 13.488 inches; or 61.9, 26.8, and 43.4 per cent. of the rainfall. The annual amount of evaporation from the bare soil is 17—18 inches; this has been a fairly constant quantity, notwithstanding great variations in the rainfall. The evaporation reaches its maximum in July, and its minimum in December; during December to March the evaporation is identical with that observed by Mr. Greaves from a water surface. There is on the whole slightly more evaporation from the deepest (60 inches) than from the shallowest (20 inches) soil. The growth of any crop would increase the amount of evaporation, and diminish the drainage.

The behaviour of soluble salts in a soil during the percolation of water has been examined. When water passes steadily through a dry soil free from fissures, it dissolves the soluble salts, and pushes this solution before it, so that, on meeting an area of discharge, the whole of the nitrates and chlorides present are expelled in a small volume of liquid. From 7 lbs. of soil thus treated more than three-fourths of the nitrates and chlorides were obtained in the first 50 c.c. of drainage. When on the other hand water is applied to a wet soil, the whole of the solution saturating the soil must be expelled to remove the salts present. The longer the operation lasts, the more water must be used, as the salts are continually redistributing themselves by diffusion. If

chlorides or nitrates are applied to the surface of a soil, and water be afterwards regularly supplied, the salts are carried downwards as a band of solution continually diffusing at its upper and lower edges. When nitrate of sodium was applied to the surface of a column of arable soil 8 inches deep, saturated with water, only a part of the nitric acid was recovered by subsequent percolation, the remainder being reduced either to ammonia or to nitrogen gas; in these experiments, the soil was always covered with water. In a similar experiment with a chloride, the whole of the chlorine was recovered.

Early analyses by Frankland of the drainage-waters from the uncropped soils forming the drain-gauges showed the presence of large quantities of nitrates. The proportion of organic nitrogen to carbon in clear waters was 1 : 2·6, in turbid waters 1 : 3·3. In the first 9 inches of Rothamsted pasture soil (roots removed) the proportion is 1 : 13; in the clay subsoil of the same land, 1 : 6. The proportion of nitrogen thus rises as oxidation proceeds.

Since May 1877, the nitric acid and chlorine have been regularly determined in mixed monthly samples of the drainage-waters from the drain-gauges. Nitrification takes place most actively in summer; the drainage-water is richest in nitrates from August to October, and poorest during the spring months. The drainage-water from the shallowest soil shows the greatest range in composition. Taking the average of four years, with an annual drainage of 17·281 inches, the amount of nitrogen as nitrates annually removed in the drainage-water has been 41·81 lbs. per acre, equal to 268 lbs. of commercial nitrate of sodium; the quantity has varied greatly with the amount of drainage. The total amount of chlorine found in the drainage-water is practically the same as that present in the rainfall.

The great loss of nitrogen by drainage from the uncropped soils of the drain-gauges, has an important bearing on the economy of bare fallow. Analyses of Rothamsted soils subjected to bare fallow show that such soils may contain, at the end of the summer, 50 lbs. per acre of nitrogen as nitrates within 20 inches of the surface; with a dry winter these nitrates will remain available for the ensuing crop, but with a wet winter a great part will be lost, and the soil suffer in agricultural condition.

III. *Drainage from Soil Cropped and Manured.*—Each plot in the experimental wheat field is furnished with a drain-pipe between 2 and 2½ feet below the surface. Analyses of the drainage-waters have been made by Voelcker (*Chem. Soc. J.*, 1871, 276), by Frankland ("Sixth Report Rivers Pollution Commission," 56—68); and since 1877, determinations of nitric acid and chlorine have been made at Rothamsted.

The drainage-water passing through a natural soil consists of—  
1. Surface-water, which passes downwards through open channels, as worm and root holes. 2. The discharge of the saturated soil. The first is much weaker than the second, save when soluble manures have been recently applied at the surface. When shallow drain-pipes begin to run, the former water preponderates in the discharge; but when the running is ceasing, the latter; the strength of the water may thus vary greatly during a single running.

The composition of the waters also varies much at different times of the year. Where diffusible salts have been applied, the drainage-water is richest shortly after their application. Ammonium salts applied to the land are at once decomposed, the acid appearing in the drainage-water as a calcium salt, while the ammonia is retained. Nitrification speedily ensues; a distinct rise in the nitrates of the drainage-water has been observed 40 hours after the application of ammonium salts. In wet weather, the nitrification of ammonia is apparently completed in a few weeks; rape-cake nitrifies more slowly. In summer, when the wheat is in active growth, the nitrates disappear in the drainage-water where no nitrogenous manure is applied, or where nitrogenous manure is applied in moderate quantity with the necessary ash constituents. Where important ash constituents (phosphates and potash) are wanting, the crop only partially assimilates the nitrates, and they continue to appear in the drainage-water. After the removal of the crop, nitrates appear in all cases in the drainage-water, and continue throughout the winter.

The average annual loss of lime and magnesia by drainage is approximately estimated as 223 lbs. per acre on the unmanured land, and 389 lbs. where 400 lbs. of ammonium salts are applied; the loss is still further increased by the application of sulphates of potassium, magnesium, and sodium; nitrate of sodium is apparently almost without influence on the loss of lime. The relative loss of magnesia and lime is about 1 : 20.

The chlorine, sulphuric acid, and soda applied in the manure are but little retained either by crop or soil, they appear in the drainage-waters in nearly the same relative proportion as they existed in the manure; sulphuric acid is more retained than chlorine or soda. Phosphoric acid and potash are very completely retained, especially the former, and appear to only a slight extent in the drainage-water. The phosphoric acid and potash unassimilated by the crop are stored in the upper layers of the soil (*Chem. Soc. J.*, 1872, 318, 837).

Approximate estimates are given of the average annual loss of nitrogen, as nitrates, by drainage in the experimental wheat field. Where no nitrogenous manure is applied, the loss is 10—12 lbs.; with 43, 86, and 129 lbs. of nitrogen applied as ammonium salts with the necessary ash constituents (the ammonia generally autumn sown) the loss has apparently been 19, 31, and 42 lbs. The loss is greater with a deficient supply of ash constituents; is greater with nitrate of sodium than with an equivalent quantity of ammonium salt; and is much greater when ammonium salts are applied in autumn than in spring.

On plots receiving no nitrogenous manure, the nitrogen annually removed in crop and drainage during 30 years is estimated as about 30 lbs. per acre; a considerable part of this has been derived from the soil, analysis of the soil showing that its nitrogen has seriously diminished during the period. Where ammonium salts or nitrates have been applied, the nitrogen of the soil has been maintained, or has suffered less diminution. The excess of nitrogen in the soil of these plots is in proportion to the weight of crop produced rather than to the quantity of ammonia applied; the nitrogen of the soil is in fact

maintained by the annual crop-residue (roots and stubble), and is proportional to its amount.

Not quite one-third of the nitrogen applied as ammonium salts, with ash constituents, has been recovered, on an average of 30 years, in the *increase* of crop obtained over the produce of ash constituents alone; this estimate takes, however, no account of the considerable alterations in the nitrogenous capital of the soil during the period, the proportion of manure nitrogen returned in the crop is thus somewhat greater than above indicated.

On plots receiving ammonium salts, the nitrogen of the manure is not fully accounted for by the nitrogen in the produce plus that estimated as lost by drainage; a part of the deficient nitrogen has been lost by the diffusion of nitrates, a loss distinct from actual drainage, a part has also possibly been lost by reduction of nitrates in the soil. On the plot manured annually with farmyard manure, a very considerable loss of nitrogen in the free state must occur. Practical conclusions are given at the end of the paper.

R. W.

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## Analytical Chemistry.

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**Method of Determining the Specific Gravity of a Liquid at its Boiling Point.** By R. SCHIFF (*Ber.*, 14, 2761—2771).—After describing some of the disadvantages attendant on the use of Ramsay's method (this Journal, Trans., 1879, 463), the author goes on to describe his own, which consists essentially in heating the liquid in an accurately graduated dilatometer to its boiling point. This is accomplished by suspending the dilatometer containing the liquid in a wide tube closed at one end, and in which some grams of the liquid are heated to boiling. When the liquid in the dilatometer has assumed the temperature of the surrounding vapour, its volume is read off on the scale of the vessel, and, after cooling, its weight determined. The volume is reduced to that at 4°, the coefficient of expansion of the glass (K) being specially determined; the correction for air expelled amounting to about 8 to 8.2 mgrms. The sp. gr. at  $t^\circ$ , water at 4° being the unit, is calculated as follows:—

$$P \cdot sp_{4^\circ}^{t^\circ} = \frac{P}{V_t(1 + K(t - 4))}.$$

$P$  = weight of the liquid (corrected);  $V_t$  = the apparent volume of the liquid at  $t^\circ$ .

A number of results are given obtained by this method, agreeing fairly well with those obtained by Kopp, Pierre, and Rosetti. In the case of the aromatic hydrocarbons, the observed molecular volumes differ from those calculated according to Kopp's law, but this difference decreases with the replacement of the hydrogen in the benzene nucleus by hydrocarbon radicles, as is shown in the following results:—

	$C_6H_6$ .	Diff.	$C_6H_5Me$ .	Diff.	$C_6H_4Me_2$ .	Diff.	$C_6H_4\left\{\begin{smallmatrix} C_3H_7 \\ CH_3 \end{smallmatrix}\right.$ .	Diff.
Found . . . .	95.94		117.98		140.2		184.39	
		3.06		3.02		2.80		2.61
$\frac{M}{D}$ calc. ac-	99		121		143		187	
cording to								
Kopp								

This difference is apparently due to the atomic volume of carbon being influenced by the manner in which the atoms are united in the benzene nucleus.

P. P. B.

**Estimation of Chlorine with the Aid of Gooch's Method of Filtration.** By D. LINDO (*Chem. News*, **45**, 193).—It is well known that silver chloride is slightly soluble in hot water; this is prevented by adding a little silver nitrate to the wash-water; the other manipulation to which the precipitate is subjected during an estimation also introduces small errors. An account of several analyses is here given, in which the loss is prevented by employing water with addition of silver nitrate, filtering through asbestos, and then drying the precipitate. The results were eminently satisfactory.

E. W. P.

**Quantitative Estimation of Chloric Acid.** (*Dingl. polyt. J.*, **243**, 499).—According to Becher (*Ber. österreich. chem. Ges.*, 1881, 110) the use of Rose's reducing agents, sulphurous acid and sulphuretted hydrogen, is not to be recommended, as the method fails to indicate the end of the reduction. The reduction of chloric acid by means of lead nitrite, proposed by Toussaint, is completed after a few minutes' heating, and gives good results. Stelling uses an alkaline solution of ferrous sulphate, but the reduction is very slow. The method works better when a neutral solution is used. The reduction with coppered strips of zinc inserted into the acid, according to Thorpe and Eccles, gives satisfactory results. It is, however, preferable to use zinc-dust free from chlorine: the reduction should be carried on in an acid solution.

D. B.

**Estimation of Sulphuric Acid.** By ZIEGLER (*Chem. Centr.*, 1882, 56).—To avoid the difficulties encountered in the filtration of barium sulphate, silver nitrate should be added immediately after precipitation of the sulphuric acid by barium chloride; a flocculent precipitate is thereby obtained, which can readily be filtered. Removal of the silver chloride is effected by ammonia without loss of the sulphate.

E. W. P.

**Separation of Quartz from Silicates.** By F. WUNDERLICH (*Ber.*, **14**, 2811—2812).—After referring to Laufer's method (this Journal, **34**, 336), which the author has found untrustworthy, as did Laufer also (*ibid.*, **36**, 79), the author states that calcined boric acid converts silica into a soluble modification.

P. P. B.

**Estimation of Phosphoric Acid.** (*Chem. Centr.*, 1882, 57.)—A committee of the agricultural research stations in Germany have drawn up a set of regulations for the estimation of phosphates.

E. W. P.

**Test-methods for Soda Works.** By G. LUNGE (*Dingl. polyt. J.*, **243**, 487—495).—For the *determination of bicarbonates* in presence of monocarbonates of the alkalis, the barium chloride method is recommended. The carbonic acid is determined in one portion of the sample, and the alkalinity in the other. By adding to a solution containing a bicarbonate a sufficient but known quantity of ammonia, the whole of the bicarbonate is converted into monocarbonate and a definite excess of free ammonia left behind. When this is treated with an excess of barium chloride, the whole of the sodium and ammonium carbonate is converted into barium carbonate, ammonium chloride, and sodium chloride. The result is that the alkalinity of the ammonium carbonate is removed, and only that of the excess of free ammonia remains. By titrating the latter and deducting the quantity obtained from that originally used, the difference will correspond with the quantity of bicarbonate originally present:  $x\text{Na}_2\text{CO} + y\text{NaHCO}_3 + z\text{NH}_3 + (x + y)\text{BaCl}_2 = (2x + y)\text{NaCl} + y\text{NH}_4\text{Cl} + (x + y)\text{BaCO}_3 + (z - y)\text{NH}_3$ .

The best method for estimating the *total sulphur in crude soda-leys* is oxidation of all sulphur compounds into sulphuric acid, and precipitation of the latter with barium chloride. The oxidation is effected by the addition of bromine-water or by the use of a solution of calcium hypochlorite.

For the *determination of potassium ferrocyanide* in soda and potash-leys, Hurter's method (*ibid.*, **237**, 311) is mostly used. Lunge, in some cases, uses the following method as a check:—The iron sulphide is removed by carbonisation, the filtrate evaporated, the residue ignited, and the iron determined in it. It is also recommended to precipitate as Prussian blue and to titrate the latter with potassium permanganate. On investigation, Lunge's method proved to be impracticable, and Hurter's method required modification. Schäppi found that the decomposition of the excess of chlorine after oxidation is a tedious operation, giving rise to inaccurate results: hence it is proposed not to add an excess of calcium hypochlorite. A weak solution (5—10 grams per litre) is run into the acidified ley from a burette, until a drop ceases to give a blue colour with ferric chloride, showing that the whole of the cyanogen is present as ferricyanide.

In *titrating calcined soda*, it is preferable to filter the solution. For determining the soluble soda in soda residues, Lunge recommends to agitate the residues with a large quantity of warm water, and evaporate the solution with previous addition of ammonium carbonate, so as to decompose the calcium salts. The residue is ignited to expel ammonia, then dissolved, filtered, and titrated. For the determination of the insoluble soda the author refers to the method described in his "Soda Industry," **2**, 422.

*Analysis of Manganese Dioxide.*—The author uses Fresenius and Will's method and the iron method. The oxalic acid method is said

to give inaccurate results when magnetic iron oxide is present, and although this is disputed by the author, the advantages of the iron method are so manifold that it is almost exclusively used at the present time. As to the influence of admixtures of sodium sulphate and chloride on the determination of the total solids in soda-leys, by means of the density, it is mentioned that the tables for  $\text{Na}_2\text{CO}_3$  indicate the total solid residue in soda-leys containing sulphate and sodium chloride.

D. B.

**Electrolytic Estimations and Separations.** By A. CLASSEN (*Ber.*, 14, 2771—2783).—This is a continuation of the method described already (*Abstr.*, 1881, 1081). In the *separation of iron and manganese*, the author recommends the addition of potassium and ammonium oxalates, and removing the iron by electrolysis, the filtrate is heated to decompose ammonium carbonate, and then manganese dioxide is precipitated by sodium carbonate and hypochlorite. Manganese dioxide often adheres to the positive electrode, and must be removed by solution in hydrochloric acid.

The separation of *iron, manganese, and phosphoric or sulphuric acid* may be effected by the same method. The iron and manganese are separated as above, and the acids are estimated in the filtrate from the manganese dioxide, phosphoric acid as magnesium ammonium phosphate, and sulphuric acid as barium sulphate. Nitrates are unsuited to electrolysis, and must be converted into chlorides.

*Iron, manganese and alumina* may also be separated by this method, the alumina being in the filtrate from the manganese dioxide. Should phosphoric acid be present with these metals, then after removal of the iron, the solution must be treated with tartaric acid, made alkaline with ammonia, and ammonium sulphide added. In this way the manganese is precipitated as sulphide. *Iron and chromium* may be separated by electrolysis of the solutions of their compound ammonium oxalates, the iron being precipitated as metal, while the solution retains the chromium as chromate. If manganese is present, it can be precipitated as dioxide after the deposition of the iron, the filtrate containing the chromates. In such cases, the manganese dioxide must be dissolved and reprecipitated, as it carries down chromium.

In the separation of *iron, chromium, manganese and alumina*, the iron and manganese are determined as before, and in the filtrate from the latter the alumina is precipitated by boiling with ammonium chloride: the filtrate from the alumina contains the chromium.

*Copper, bismuth, cadmium, nickel, cobalt and zinc*, may be each separated from manganese in the same manner as iron.

*Iron and glucinum* may be separated by depositing the iron from the mixed solutions, containing an excess of ammonium oxalate, by a feeble current. When a strong current is used, the solution becomes hot and glucina separates out, otherwise there is no difficulty attending this separation.

In separating *iron, glucinum, and aluminium*, the solution after removal of the iron is poured into another platinum dish, and the electrolysis continued to precipitate the alumina. The filtrate from the latter yields glucina on boiling.

*Zirconium* and *vanadium* may be separated from iron in the same manner as glucinum. P. P. B.

**Separation of Gallium.** By L. DE BOISBAUDRAN (*Compt. rend.*, **94**, 1154—1155).—Cupric or cuprous oxide may be used with advantage instead of barium carbonate or lime for the precipitation of gallium in presence of zinc and iron. The excess of copper is easily removed by means of hydrogen sulphide, the solution being made strongly acid in order to prevent gallium being carried down with the copper sulphide. When iron is present, it is first reduced by boiling with finely divided copper, and the cuprous oxide then added. It is almost impossible to prevent oxidation of some of the iron during filtration, and the treatment must therefore be repeated several times. The cuprous oxide precipitated by glucose answers very well if carefully washed to remove every trace of organic matter.

Metallic cadmium precipitates gallium oxide from a solution of gallium chloride mixed with zinc chloride after *prolonged* boiling, but the precipitation is not complete.

Cupric oxide may be used with advantage in place of carbonates of the alkaline-earth metals for the separation of alumina and the other higher oxides from protoxides, and the combined action of metallic copper and cuprous oxide may be useful in the analysis of mixtures of ferric and aluminium oxides. C. H. B.

**Estimation of Phosphorus in Iron.** By J. L. SMITH (*Chem. News*, **45**, 195).—The following is the most accurate method of estimating phosphorus in pig-iron. One gram of the iron is heated on a water-bath with 3—4 c.c. water and 10—15 c.c. aqua regia added gradually.

When the liquid has evaporated, the residue is heated in an air-bath at 150° for an hour, then 3—4 c.c. hydrochloric acid are added, and the whole, having been filtered to remove silica, is made up to 100 c.c. with water. Using 90 c.c. of solution, and diluting with 100 c.c. water, the ferric salt is now reduced by sodium or ammonium sulphite, and ammonia is added to faintly alkaline reaction, when 20 c.c. acetic acid and ammonium acetate are added; finally, the 10 c.c. of the original solution are added with 200—300 c.c. water. The whole solution is then boiled for an hour, and a basic ferric salt containing all the phosphorus is formed. To separate the phosphorus, the basic salt, after being filtered off, is dissolved in nitric acid; if titanium be present, a flocculent precipitate will remain, which must be removed. The acid solution of the nitrate must be neutralised with ammonia, and 30 c.c. molybdic acid solution added.

The precipitated double salt should be dried at 120 c.c. and weighed on the filter.

Cold-shortness of iron has been attributed to the presence of phosphorus, but the author does not wholly agree with this theory, although phosphorus may have some influence. E. W. P.

**Volumetric Estimation of Lead by Potassium Permanganate.** By H. JÜPTNER (*Chem. Centr.*, 1882, 58).—Haswell's process, founded

on the formation of  $5\text{PbO}_2 \cdot 2\text{MnOK}_2\text{O}$ , when potassium permanganate is introduced into a solution of lead nitrate mixed with potash, ammonia or zinc oxide, gives most accurate results; when the brown precipitate sinks there is no difficulty in perceiving the tint of excess of permanganate. 5 mols. lead nitrate require 1 mol. permanganate. The titration is not affected by alkalis or alkaline earths, or by the metals of the iron group. Bismuth should be removed as basic nitrate, and copper by reason of its strong colour, must be separated by the aid of ammonia and its carbonate, the precipitate being dissolved in nitric acid previous to titration. E. W. P.

**Behaviour of Lead Chromate in Organic Combustions.** By H. RITTHAUSEN (*J. pr. Chem.* [2], 25, 141—143).—Commercial lead chromate when heated by itself is often found to give off gases absorbable by potash solution and calcium chloride: it may be purified and regenerated after use, by igniting the chromate in a stream of oxygen, which gas is absorbed until complete regeneration ensues. The author recommends that this should be done before every combustion. J. K. C.

**Estimation of Glycerol.** (*Dingl. polyt. J.*, 243, 499).—Glycerol mixed with volatile solvents is often determined by heating at  $100^\circ$  to  $110^\circ$  until the residue ceases to lose more than 1 mgrm. per hour, while others mention that on heating for 8 to 10 hours at  $100^\circ$  to  $110^\circ$ , it is completely volatilised.

Couttolenc (*Bull. Soc. Chim.*, [2], 36, 183) finds that glycerol is obtained in the anhydrous state when heated for five hours at  $90^\circ$ , but at this temperature a surface of one square centimeter is said to lose 3.17 mgrms. glycerol. According to Barbsche (*Chem. Centr.*, 1881, 208), two drops of phenol in 8,000—10,000 parts of water gives a distinct blue coloration with one drop of a solution of ferric chloride, which is destroyed by the addition of 6—8 drops of glycerol. This reaction is recommended for detecting glycerol in wine and beer.

It is shown (*Pharm. Centralhalle*, 1881, 164) that the same reaction is obtained with sugar, gum arabic, &c., hence its application for detecting glycerol in wine and beer is not practicable. D. B.

**Analysis of Beet-root and Sorghum.** By CASAMAJOR (*Chem. News*, 45, 191—193).—Unsuccessful attempts have been made in America of late years to manufacture sugar from beet-root and sorghum, and the estimates of the value of either sources differ widely. The object of the present communication is to point out the processes whereby the quantity of sugar obtainable from a given weight of material can be ascertained beforehand. From a given quantity of raw sugar, a certain portion of pure sugar can be obtained, as well as molasses which will not yield crystallisable sugar, and if the total sugar and that in molasses be known, then the pure sugar can be calculated. The composition of molasses is generally constant, having a density =  $40^\circ$  Baumé, and consisting of sugar = 37.5, soluble impurities, 37.5, and water 25 per cent. When comparing the products obtained at different factories, the results are generally

stated in the dry state, and the quantity of sugar in the dry product compared with the total substance is called the coefficient or quotient of purity. In the case above quoted, the quotient is 50, implying that in cane-sugar 1 per cent. of impurities prevents the crystallisation of 1 per cent. sugar. Applying this information to a sugar whose coefficient is 92, *i.e.*, there are 8 parts of impurities present, the yield of pure sugar would be  $92 - 8 = 84$  per cent. In beet-root sugar, 1 per cent. impurities prevents the crystallisation of 1.2 of sugar. The composition of sorghum molasses has not as yet been determined. The process for ascertaining the quotient of purity has been described (*Amer. Chim.*, 1873), and gives satisfactory results. The outline of the process is that the pure sugar in 100 c.c. is given by multiplying the indication of the saccharometer by 0.26048 for Ventzke's instrument, by 0.1635 for Duboscq's; the total matter in solution is found by multiplying degrees Balling by sp. gr.: then the quotient is found by dividing the first by the second quantity.  $S =$  saccharimetric test,  $P =$  sp. gr., and  $B =$  Balling degrees, then quotient  $= \frac{S \times 0.26048}{B \times P}$ . In the articles above referred to, factors

are given for the simplification of this calculation, so that the sp. gr. may be introduced. The samples for testing should be wedges, the angles at the base being equal, and the apex being at the centre of the root; the juices obtained by grating and pressing should be neutralised with lime, heated and filtered. The juice from sorghum cane is easily obtained by wringing it with the hands: the water in the juice is found by taking the difference between 100° and the Balling degree. A specimen of sorghum juice had as quotient 44, therefore no sugar could be manufactured from it. E. W. P.

**On Milk and Butter.** By M. SCHMÖGER and others (*Bied. Centr.*, 1882, 276—279).—Schmöger considers that 3.5 per cent. butter is too high an estimate for morning milk, as in his experiments with 45 cows he has only obtained 2.8 per cent. Concerning the analysis of milk, he finds that in no case did the sp. gr. fall below 1.029, but in 80 out of 3000 cases it rose to 1.033, and in three cases to 1.034; the results from the creamometer are of small value, although the instrument may be useful to the farmer within certain limits; the minimum of fat in milk is 2.5 per cent. In a case reported by Fleischmann, in which butter would not come in a specimen of milk, the cause was that the temperature was too low. E. W. P.

**Estimation of Alkaloids in Cinchona Barks.** By KISSEL (*Chem. Centr.*, 1882, 60).—The method suggested by Prollius (this vol., 246) is very accurate, but the ether process is better than the alcoholic. Prollius is in error in believing that the alcohol method leaves a residue containing all the alkaloids, and that by the ether method only quinine and its homologues which are soluble are obtained. It is generally supposed that ether removes only quinine from the bark, as the other alkaloids when once separated are very difficult of solution, but this is not the case, as the alkaloids are completely extracted by the ether. E. W. P.

**Potassiobismuthous Iodide as a Test for Alkaloids.** By F. MANGINI (*Gazzetta*, 1882, 155—157).—Dragendorff, in his Manual of Toxicology, recommends this compound as one of the most delicate tests for alkaloids, but adds that it cannot be employed to distinguish one alkaloid from another, as it gives orange-coloured precipitates with most of them. The author of the present paper, however, finds that the characters of this reagent vary considerably according to the manner in which it is prepared. When obtained by Russland's process, described by Dragendorff, it produces a turbidity even in pure water; but when prepared by mixing 3 pts. potassium iodide with 16 pts. liquid bismuth iodide and 3 pts. hydrochloric acid, it does not give any turbidity with water, and is an extremely delicate test for alkaloids, serving also to distinguish many of them one from the other by the various gradations of colour of the precipitates and their alterations after long standing.

The following are the results obtained :—

*Strychnine* : light yellow precipitate becoming dark yellow after some time; supernatant liquid remains clear.

*Morphine* : reddish-yellow precipitate which agglomerates at the bottom; liquid remains clear, precipitate disappearing after a few days if the whole is left at rest, and the liquid becoming canary-yellow.

*Codeine* : immediate, copious, yellowish-red precipitate, remaining for some time suspended in the liquid, and assuming a light brick-red colour when left at rest.

*Atropine* : precipitated at first in filaments, but gradually settling down in the form of a reddish-yellow powder, which if left at rest becomes canary-yellow, and dissolves after some time, colouring the liquid golden-yellow.

*Aconitine* : precipitated at first in flocks, but suddenly forms at the bottom a chrome-yellow pulverulent precipitate, which does not change colour when left at rest, whereas the liquid becomes yellow.

*Brucine* : precipitated at first in filaments which ultimately settle down with gold-yellow colour, becoming paler when left at rest for some time.

*Nicotine* : immediate red pulverulent precipitate, which suddenly falls to the bottom, and becomes reddish-yellow when left at rest.

*Cicutine* : precipitate similar in character but of darker colour, and becoming dirty-white when left at rest.

*Solanine* : slowly precipitated with lemon-yellow colour, becoming darker on repose and adhering to the bottom of the tube when shaken.

*Veratrine* : light yellow precipitate forming slowly, remaining suspended for some time, and becoming light canary-yellow when left at rest.

*Narceine* : light yellow precipitate forming slowly and remaining suspended like that of veratrine, but of deeper colour; becomes reddish-yellow on repose.

*Quinine Sulphate* : immediate brick-red precipitate which suddenly falls to the bottom, and becomes dirty-yellow on repose; remains suspended after agitation.



*Cinchonine Sulphate*: like the last, but does not fall down so quickly, and acquires a darker colour when left at rest. H. W.

**Detection of Urea by Oxalic Acid.** By E. BRÜCKE (*Monatsh. Chem.*, 3, 195—196).—Oxalic acid is commonly regarded as inferior to nitric acid as a test for urea, but the mode of applying it may be considerably improved by taking advantage of the sparing solubility of urea oxalate in a mixture of alcohol and ether. A still better method, however, is to heat the alcoholic extract supposed to contain the urea with a small quantity of amyl alcohol, and treat the solution, decanted or filtered if necessary, with a cold saturated solution of oxalic acid in amyl alcohol. The urea oxalate is then precipitated in small crystals, but may be obtained in larger and better defined crystals, fit for microscopic examination, by warming the liquid till the crystals are redissolved, and leaving it to cool. Another mode of proceeding is to add the oxalic acid in the solid state, then heat till it is all dissolved, and leave the solution to cool. The advantage of this method is that it does not unnecessarily increase the quantity of liquid; it is necessary, however, to avoid adding too much oxalic acid, as an excess would crystallise out as such on cooling. The solution of urea in amyl alcohol may also be mixed with a solution of oxalic acid in anhydrous ether. Precipitation then takes place quickly and abundantly, but the crystals are mostly small and ill-defined, so that it is not easy to recognise them. This mode of proceeding may, however, be recommended when complete precipitation is desired, as for quantitative estimation. In such cases also, the oxalic acid may be added in substance, the whole heated to obtain large crystals, and the excess of oxalic acid finally removed by anhydrous ether. Should the urea be found in excess instead of the oxalic acid, the precipitation must be completed by means of an etheric solution of oxalic acid.

The amyl alcohol used in this reaction must be so far pure as not to turn red or brown when the oxalic acid is dissolved in it. A moderate quantity of ethyl alcohol does not interfere much with the reaction, but nevertheless its absence is desirable. H. W.

**Quantitative Estimation of Albuminoids and Non-albuminous Matter in Plants.** By E. SCHULZE (*Landw. Versuchs.-Stat.*, 27, 449—465).—This paper is principally a review of the methods employed for the estimation of the nitrogenous matter in plants, and is followed by an answer to a paper of Kettner's on the question of priority of introduction of the various processes. Schulze considers that it is quite unnecessary to estimate the ammonia originally present in fodder before determining that produced by decomposition of the amides, as the quantity is so small, and it is enough to estimate the total ammonia produced by boiling the extract with dilute acid, and to determine the nitrogen set free by nitrous acid; a sketch of a simple piece of apparatus for collecting the ammonia set free by magnesia is given. Doubt has lately been thrown on the exactness of the figures obtained by Sachsse's method, but the author considers that the results are perfectly trustworthy so long as asparagine, glutamine, and

primary amido-acids alone are present. Uncertainty enters only when the nitrogenous matters which cannot be separated by precipitation from the above are present, and then it is possible that they are partially decomposed by the nitrous acid; such a substance is allantoin, but up to the present time it has been found in only one plant (plantain), although it may exist in others. The conclusion which may, therefore, be drawn from results obtained by Sachsse's method of estimation, is that the nitrogen present represents the maximum amount of asparagine, glutamine, and amido-acids that could possibly be present. Mayen (*Zeits. Anal. Chem.*, **20**, 37) believes that the azotometric method of estimating amides is impracticable; with this statement, the author cannot agree, as having made experiments with pure asparagine, he finds the results accurate; even if the azotometric process were useless, there is still Schlösing's method, which is often preferable, as when much glutamine is present. E. W. P.

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### Technical Chemistry.

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**Gelatino-bromide Emulsion.** By PLENER (*Photographic News*, 1882, 257).—This is a short account of a patent recently taken out by Plener for separating the sensitive silver bromide compound from the emulsion, and, after washing it, again mixing it with fresh gelatin. This is done by placing the melted emulsion in a metallic vessel of the shape of a truncated cone, silver-plated inside, which is then made to rotate at a very high speed (4000 revolutions per minute for a vessel one foot in diameter) for about ten minutes, keeping the gelatin emulsion from setting by heating the vessel externally. In this way, the solid sensitive silver compound is deposited on the circumference of the bottom of the vessel, and the clear gelatin solution may be syphoned out. The silver compound is then mixed with warm water by the aid of a brush, again separated by rotating the vessel, and the operation repeated until all traces of gelatin and soluble salts have been removed. The purified sensitive silver compound can then be mixed with fresh gelatin, collodion, &c., for preparing sensitive plates.

The important feature in the process is that it allows of fresh undecomposed gelatin being substituted for that which has been decomposed by heat, &c., in the preparation of the original emulsion, and thus greatly diminishes or entirely removes the tendency to green fog and frilling. Moreover, the original emulsion may be diluted to any extent, or any desired proportion of gelatin may be employed, so that the sensitive silver compound may be obtained in the most advantageous state of division, and can subsequently be incorporated with the proper proportion of fresh undecomposed gelatin. C. E. G.

**Absorption of Volatile Bodies by the Aid of Heat.** By T. SCHLOESING (*Compt. rend.*, 94, 1187—1189).—Bodies in a truly

gaseous condition are readily absorbed when passed over some absorbing material, by virtue of the mobility of their molecules, but substances mixed with gases in the form of finely divided solid particles or of liquid spray, are only partially absorbed, because the particles have not the required mobility and rate of diffusion. If, however, the gas containing the solid or liquid particles in suspension is heated to such a temperature that the particles are rendered gaseous, then they can be readily absorbed. The author has adopted this plan with success on a manufacturing scale. If air mixed with hydrochloric acid is simply heated to 100° by means of steam, the acid can be completely absorbed by a much smaller volume of water than is ordinarily used, even when the percentage of hydrochloric acid in the gas is but small. In this way, a highly concentrated aqueous solution of the acid can be obtained. The same temperature is sufficient to produce, by dilute sulphuric acid, the complete and almost instantaneous absorption of ammonium carbonate suspended in air.

C. H. B.

**Purification of Soda-leys with Zinc.** By K. W. JURISCH (*Dingl. polyt. J.*, **244**, 71—79).—All crude soda-leys produced by the Leblanc process contain sodium sulphide. In working up these leys for soda this impurity must be removed. Hitherto the following methods have been used:—(1.) Oxidation of the caustic leys and of the fused caustic soda with Chili saltpetre. (2.) Oxidation of the fused caustic soda with air. (3.) Carbonisation and oxidation of the crude leys with carbonic anhydride and air. (4.) Oxidation of the leys with air, with or without the use of Pauli's method, and subsequent oxidation of the concentrated caustic leys, and of the melt with Chili saltpetre; and (5.) Precipitation with zinc. The first four methods lead to the same end, namely, the conversion of sodium sulphide into sulphate, which of course reduces the percentage of total alkali in the finished product. The last-named method has the advantage that by precipitating the sulphur of the sodium sulphide as zinc sulphide, its sodium equivalent remains in the caustic soda produced, so that by this process soda of higher percentage may be obtained. A number of experiments have been made at the Widnes works of James Muspratt and Sons, with a view of ascertaining how the cost of the working of this method compares with the cost of the oxidation method by means of air and saltpetre. It is shown that the cost of lixiviating with zinc is covered by the value of the additional alkali produced, and that a saving of 11.64 marks per ton of caustic soda (70 per cent.) is realised in comparison with Pauli's oxidation method, and subsequent oxidation with saltpetre.

D. B.

**Solubility of Calcium Aluminates in Water.** By E. LANDRIN (*Compt. rend.*, **94**, 1054—1055).—The author finds that calcium aluminates are soluble in water to a relatively considerable extent. It follows, therefore, that the presence of these compounds is injurious to the setting properties of hydraulic mortars, and that materials which form no soluble aluminates are best adapted for the preparation of such mortars. Ferric oxide forms no compounds with lime analo-

gous to calcium aluminates. The author suggests that the solubility of the calcium aluminates may be utilised in the manufacture of sugar and the treatment of molasses.

C. H. B.

**New Process for Extracting Copper from Copper Pyrites.** By R. FLECHNER (*Dingl. polyt. J.*, **243**, 482—487).—The author has worked this process successfully for the extraction of copper from the Balán ores (Balán, near Czik-Szent-Domokos, in Transylvania), which consist of copper pyrites associated with iron pyrites. Magnetic pyrites is present only in minute quantities. This circumstance, combined with the absence of calcium salts in the ore, imparts to it the property of being partly decomposed by atmospheric influences, resulting in the formation of copper-salts. It is difficult to obtain the copper from the poorer kinds of ore, as these, being imbedded in quartz and chlorite, adhere firmly to the ore; and it was especially with a view of surmounting this difficulty that the author undertook this work. At the end of 1880 no profit was attached to the working of these mines, but they now give a good revenue, and owing to the abundance of unextracted ore, a good future has been secured.

The author's process is mainly a "sulphating" roasting process, and although metallurgically it presents no novelty, its practical application is new. The ore is freed from gangue, so that the raw material contains about 2 per cent. of copper. It is broken up in pieces of the size of a nut, arranged in open kilns of 38—40 tons, within a few feet of the main adit level for carrying out the ore, and subjected to a moderate preliminary roasting, occupying 12—14 days. A charge of 40 tons requires 1 cubic meter logs, 0.3 cubic meter charcoal, and a labourer working for six days. The roasted ore is then ground in a crushing mill. Two men grind 14—16 tons of ore in twelve hours. The ground ore is spread out in masses of 300 k., mixed with iron sulphate liquor to the consistence of mortar, then heaped up in piles of 15—20 tons, and allowed to remain for a few days. The liquor used for lixiviating the ore is obtained as a bye-product. Two men lixivate 8—10 tons of ore in twelve hours; the lixiviated material is then brought in trucks to the gas furnaces. The author uses two gas reverberatory furnaces, worked with one gas generator and four men. The material is heated for six hours, then taken in trucks to the lixiviating tanks. These are arranged in five groups, each group having five tanks of 3 cubic meters capacity. The tanks are placed over each other, and side by side, in the following manner:—The uppermost tank is used for receiving the weak iron liquors or washings. Under the two ends of this tank, and at a depth of the height of the same, two tanks are placed for receiving the ore, between these, and at a correspondingly lower depth, there is a tank for collecting the copper solution, and under this, at a similar distance apart, a precipitating tank is placed.

In conclusion, the author describes the mode of procedure of the whole process more fully. From the precipitating tanks, a product is obtained, containing in its dry state between 94 and 96 per cent. copper, 2—4 per cent. iron, and 3—4 per cent. silicates. The cementation copper is sifted, formed into blocks weighing 25 k., dried and refined.

It is mentioned that this process may be advantageously used for the extraction of copper from antimonious copper-ores or fahl-ores, containing at least 5—8 per cent. copper, and a large amount of quartz gangue. D. B.

**Improvements in the Manufacture of Wine.** By F. A. REIHLEN (*Bied. Centr.*, 1882, 273—275).—Reihlen has patented a process in which the pressed grape skins are to be boiled with water so as to rupture the cells containing the colouring and aromatic matter which, forming a fermenting and colouring extract, cause the fermentation of the must to be clear, and without the unpleasant taste usually imparted to the wine by the ferment. L. Weigert, remarking on the above patent process, thinks that although the extract from the skins feeds the ferment, yet there is no great gain obtained; still, when black grapes are so treated the wine is four to six times darker. L. Rosler considers that it is only a ferment in the skins, and not the skins themselves which cause the fermentation. E. W. P.

**Sugar Manufacture without Animal Charcoal and with Sulphurous Anhydride.** By G. F. MEYER (*Bied. Centr.*, 1882, 279—281).—When the yield of sugar from beet is good, the use of animal charcoal can be dispensed with for the purification of the sugar separated from lime; any mechanical impurities may be removed by filtration through fine sand. Sulphurous anhydride may be used to decolorise without raising the percentage of sulphates. A. Reinecke describes a process in which sulphurous anhydride and then steam is passed into the lime solution of sugar, whereby a precipitate is formed which carries down all colouring matter. E. W. P.

**Preparation of Soft Soap.** (*Dingl. polyt. J.*, 244, 56—64.)—According to Ringel (*Seifenfabrikant*, 1881, 82), pure soft soap consists mainly of potassium oleate, potassium carbonate, and the salts contained in the potash used for its preparation. Pure potassium oleate obtained from soft soap by treatment with potassium chloride, is a firm, tough, slightly translucent mass. Soft soap does not acquire its translucent appearance and ductile character until after the addition of a solution of caustic and carbonated alkali. Instead of finishing soaps with potash, potassium chloride, sulphate, borate, silicate, &c., may be used; sodium salts, however, produce soaps of less perfection. These salts have the property of causing the soap to combine with water; 100 parts of water require 12—15 parts of these salts to effect this combination, so that no watery particles separate on cooling.

For the preparation of green soft soap Starke (*Seifenfabrikant*, 1881, 83) uses hempseed oil, linseed oil, and olein. The fat is introduced into the copper, mixed with an equal weight of ley of 18° to 20° B. ( $\frac{2}{3}$  potash-ley and  $\frac{1}{3}$  soda), agitated repeatedly, allowed to settle until the next day, and then heated to boiling. Combination soon takes place, and may be recognised by the absence of oil, which at the

commencement floated on the surface of the ley, and by the fact that a sample placed on the tongue no longer tastes of alkali, but has a sweetish taste resembling oil. The mixture is now subjected to gentle boiling, and treated gradually with ley of  $20\text{--}24^{\circ}$  B. until a transparent emulsion is produced. At this period, the fire is increased and the boiling continued until the soap shows large lamellæ on the sides of the copper, and only very little froth is produced. The soap when finished should remain clear on cooling.

According to Eichbaum (*Seifenfabrikant*, 1881, 85), one of the best soft soaps is the so-called "natural grain-soap," which is made from potash-ley (containing not more than 5 per cent. of soda) and German linseed oil. Saponified oleïn and twice purified cotton-seed oil are used in some cases.

Seidemann (*Seifenfabrikant*, 1881, 153) describes the preparation of transparent glycerol soft soap. The oils used for the manufacture of this soap must be bleached. In other respects the preparation resembles that of other soft soaps. The bleaching is effected in the following manner:—The oil is heated with direct steam and mixed with 5–8 per cent. of potash-ley of  $28^{\circ}$  B. It is agitated thoroughly, then allowed to remain quiescent. The precipitate which subsides is used for the manufacture of darker-coloured soft soaps.

In order to prevent the freezing of transparent soap, it is recommended to use linseed oil in its preparation. For washing woollen goods, Menzies (*Seifenfabrikant*, 1881, 169) recommends the use of neutral potash soap, which is said to supersede soda soaps.

D. B.

### **Presence of Nicotine in Tobacco-smoke, and Consideration of the Active Poison in the Combustion-products of Tobacco.**

By R. KISSLING (*Dingl. polyt. J.*, 244, 64–71).—Having recognised the toxic nature of nicotine and its action on the nervous system, and the relatively considerable quantity of this alkaloid present in tobacco, it was obviously interesting to ascertain what influence the most important consumption of tobacco, viz., smoking, has on nicotine. Although the number of investigators on this subject is very limited, a complete series of chemical and physiological facts can nevertheless be quoted. Whilst a few investigators indisputably deny the presence of even traces of nicotine in tobacco-smoke, others maintain with equal certainty that it exists in considerable quantity. The author has collected these facts, and the present paper is devoted to a critical discussion of the same, and simultaneously to an account of his own investigations. The following are the details of the principal publications on this subject:—Unverdorben (*Pogg. Ann.*, 1826, 8, 399) investigated the products obtained by the dry distillation of tobacco. He obtained (1) an ethereal oil; (2) an oily acid; (3) an empyreumatic acid; (4) a reddish-brown resinous substance, soluble in potassium hydroxide; (5) a trace of a powdery substance, insoluble in potash and in acids; (6) a small quantity of picoline; (7) a base soluble in water, having a burning taste and unpleasant pungent smell, causing choking; (8) fuchsine; (9) a body resembling the latter; and (10) two extractiform bodies.

Zeise (*Annalen*, **47**, 212) was the first who passed tobacco-smoke from a pipe through an aspirator. He found the following constituents:—A peculiar empyreumatic oil, butyric acid, carbonic anhydride, ammonia, paraffin, empyreumatic resin, water, a small quantity of acetic anhydride, carbonic oxide, and carburetted hydrogen gas.

Melsens (*ibid.*, **49**, 353) has investigated the condensation-products of tobacco-smoke with the view of proving the presence of nicotine. He isolated nicotine from this mixture of empyreumatic, oily, tarry, and resinous products, and obtained numbers agreeing with the formula  $C_{10}H_{14}N_2$ ; 4.5 k. of smoked tobacco yielded 33 grams of nicotine.

Vohl (*ibid.*, **148**, 231), in conjunction with Reichshauer, found sulphuretted hydrogen and hydrocyanic acid in tobacco-smoke. Vohl and Eulenberg (*Vierteljahrsschr. f. gerichtl. und öffentl. Medecin*, New Edition, **14**, 249) conclude that nicotine in tobacco is completely decomposed by the smoking process, and that the intense action of tobacco-smoke on the nervous system is attributable to the presence of pyridine bases. The following pure substances were isolated:—A hydrocarbon of the formula  $C_{38}H_{18}$ ; pyridine,  $C_5H_5N$ ; picoline,  $C_8H_7N$ ; lutidine,  $C_7H_9N$ ; collidine,  $C_8H_{11}N$ ; parvoline,  $C_9H_{13}N$ ; coridine,  $C_{10}H_{15}N$ ; rubidine,  $C_{11}H_{17}N$ ; and viridine,  $C_{12}H_{19}N$ . The presence of the following substances was also established:—Carbonic anhydride, hydrocyanic acid, sulphuretted hydrogen, formic acid, acetic anhydride, propionic acid, butyric acid, valeric acid, carbolic acid and creasote, several hydrocarbons of the acetylene group, finally ammonia, methane, and carbonic oxide. The presence of caproic, caprylic, and succinic acids could not be determined conclusively.

Heubel (*Centralbl. med. Wissensch.*, 1872, 641) has made numerous physiological experiments on tobacco. He concludes that—(1) nicotine is unmistakeably contained in tobacco-smoke; (2) by the slow combustion of the nicotine in tobacco, a large quantity is found in the smoke; (3) the fact that in spite of its great volatility and tendency to decomposition, nicotine is largely contained in tobacco-smoke, is explained by the leaves and the smoke containing this alkaloid as a stable salt, and not in the free state.

Le Bon (*la Fumée du Tabac, Recherches Chimiques et Physiologiques*) has found the following constituents in tobacco-smoke:—Nicotine, ammonia, carbonic oxide, hydrocyanic acid, and two aromatic (not in a chemical sense) substances, one of which is collidine.

Pease (*Jour. Amer. Chem. Soc.*, **2**, 338) analysed the smoke from 3.6685 grams Havannah tobacco by burning the latter in a long wooden pipe, and passing the smoke through two bottles containing water acidified with sulphuric acid. The filtered and concentrated solution was then titrated with potassiomeric iodide. He obtained 0.081 gram nicotine.

In discussing these facts, the author mentions that, of the two bases found by Unverdorben in addition to picoline, one probably was nicotine. Zeise's investigations are of great importance. It cannot be disputed that by the dry distillation of tobacco, other products are formed than by the smoking process, as in the latter case a constant or intermittent current of air passes through the tobacco. Referring to Melsens' researches, the author mentions that he is the only inves-



tigator who has conclusively established the existence of nicotine in tobacco-smoke. The quantity of this alkaloïd amounts to about 0·7 per cent. of the weight of tobacco consumed, and about 15 per cent. of the total quantity of nicotine contained in tobacco. In conclusion of the first part of his paper, the author criticises the researches of Vohl, Heubel, Le Bon, and Pease. He shows that Vohl's opinion as to the non-existence of nicotine in tobacco-smoke is without foundation. This chemist evidently disregarded the fact that nicotine is decomposed by warm potassium hydroxide. The remaining three publications cannot be regarded as a satisfactory solution of the whole question of controversy of opinion, as they are very incomplete.

D. B.

**Use of Algarobilla in Tanning.** By W. EITNER (*Ding. polyt. J.*, **244**, 89).—Algarobilla is the fruit of the *Balsamocarpum brevisolium*, a tree growing in Chili. The pericarp of this fruit is 3 to 3·5 cm. long, contains 40—50 per cent. tannin, and resembles the fruits of Divi, Bablah, and Neb-Neb used in tanning. The seeds, which amount to about 17 per cent. of the weight of the entire fruit, are dark-coloured, hard, and free from tannin. Owing to the fact that the tannin exists in the algarobilla in the free state, and therefore dissolves readily in water, and that the solution has a light yellow colour, this fruit forms a valuable tanning agent; but as the extract is practically a pure solution of tannin—which does not give a serviceable leather—it must be used with other tanning substances to increase the percentage of tannin.

D. B.

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## General and Physical Chemistry.

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**Molecular Refraction of Liquid Carbon Compounds.** By H. LANDOLT (*Ber.*, 15, 1031—1040).—Two years ago A. Lorentz and H. Lorenz came to the conclusion independently that the relation between the velocity of transmission of light and the specific gravity of a substance can be expressed by the formula  $\frac{n^2 - 1}{(n^2 + 2)d} = C$  (in which  $n$  is the index of refraction, and  $d$  the sp. gr.), instead of the formula  $\frac{\mu - 1}{d} = C$ , which has been adopted hitherto. It was formerly shown by the author that the refraction-equivalent of a mixture or compound is the sum of the refraction-equivalent of its components, a relation which is expressed by the formula  $\frac{N - 1}{D} (p + p_1) = \frac{n - 1}{d} p + \frac{n_1 - 1}{d^2} p_1$ , in which  $N$  is the index of refraction,  $D$  the sp. gr. of the mixture,  $n$ ,  $n_1$ , and  $d$ ,  $d_1$ , are the same values for the components, and  $p$ ,  $p_1$  their relative weights. The author finds that the equation  $\frac{N^2 - 1}{(N^2 + 2)D} (p + p_1) = \frac{n^2 - 1}{(n^2 + 2)d} p + \frac{n_1^2 - 1}{(n_1^2 + 2)d_1} p_1$  gives results which do not differ materially from those obtained by the former equation, and that the calculated differ from the observed results only in the fourth place of decimals, except in cases of mixtures of such strongly refractive liquids as carbon bisulphide, benzaldehyde, &c. According to the former equation, with the aid of Cauchy's dispersion formula, the refraction-equivalent for the hydrogen line  $H_a$  is (I)  $P \frac{n_a - 1}{d} = M_a$  and  $P \frac{A - 1}{d} = M_A$ , but according to the latter for the same line (II)  $P \frac{n_a^2 - 1}{(n_a^2 + 2)d} = M_a$  and  $P \frac{A^2 - 1}{(A^2 + 2)d} = M_A$ . A comparison of the values obtained by Equation II for the molecular refraction of various substances, which are about one-third less than those obtained by Equation I, yield to analogous relations between chemical composition and optical activity.

(1.) Isomeric compounds, whose carbon and oxygen atoms are attached by single bonds, possess the same refraction-equivalent; but this is not the case with metameric compounds of different chemical composition, as allyl alcohol and propaldehyde.

(2.) Similar differences in empirical formula correspond to similar differences in refraction-equivalent; these differences are given in the table below, and are expressed for Equation I by  $r_a$  and  $r_A$ , and by  $r_a$  and  $r_A$  for Equation II.

	$\frac{n-1}{d}$		$\frac{n^2-1}{(n^2+2)d}$	
	H <sub>α</sub> .	A.	H <sub>α</sub> .	A.
Singly-bound carbon-atom .....	5.0	4.86	2.48	2.43
Hydrogen .....	1.3	1.29	1.04	1.02
Singly-bound oxygen-atom O' ....	2.8	2.71	1.58	1.56
Double-bound oxygen-atom O'' ....	8.4	3.29	2.34	2.29
Chlorine .....	9.8	9.53	6.02	5.89
Rise for each doubly-bound carbon-atom .....	2.4	2.0	1.78	1.69

Thus according to Lorenz's formula the refraction-equivalent of a compound can be calculated from those of its components by the equations—

$$R_{\alpha}(C_a H_b O''_c O'_d) = 2.48 a + 1.04 b + 2.34 c + 1.35 d$$

$$R_A(C_a H_b O''_c O_d) = 2.43 a + 1.02 b + 2.29 c + 1.56 d$$

The calculated and observed values are given in an extensive table in the original memoir. V. H. V.

**Dependence of the Molecular Refraction of Liquid Carbon Compounds on their Chemical Constitution.** By H. SCHRÖDER (*Ber.*, 15, 994—998).—The author has collected the values of the refraction-equivalent of organic substances from A. Lorentz and H. Lorenz's formula  $\frac{\mu^2-1}{(\mu^2+2)d} = C$ . He confirms the results of Landolt (see last Abstract), Wiedemann, and others, that this formula deduced from theoretical considerations of the electromagnetic and ether theories leads to the same uniformities between chemical composition and refraction of light as the empirical formula  $\frac{n-1}{d} = C$ .

The following results for the hydrogen lines H<sub>α</sub> and H<sub>γ</sub> are noted:—

- (1.) The refraction equivalent increases with the molecular weight.
- (2.) The groupings CO, CH<sub>2</sub>, O'' (as the two oxygen-atoms of the carboxyl group of the acids), OH<sub>2</sub>, of the alcohols produce the same effect on the refraction-equivalent, but the O atom of the hydroxyl group has only one-third the effect of the previously named groups, hence it follows that in saturated compounds the atom-refractions of carbon, hydrogen, and singly bound oxygen are equal; this atom refraction the author calls the "refraction stere;" and the refraction of the doubly-bound oxygen-atom is equal to two steres. The value of a refraction stere is about 1.47. In a series of tables the refraction equivalents of the fatty acids and their corresponding aldehydes are given for the lines H<sub>α</sub> and H<sub>γ</sub>, those of the former differing from those of the latter by one refraction stere. A few examples are here adduced to illustrate the author's method:—

Substance.	Formula and No. of refraction steres.	Refraction-equivalent for $H_\alpha$ .
{ Acetic acid . . . . .	$C_2^2H_4^4O_2^3$	$12.93 = 9 \times 1.437$
{ Ethaldehyde. . . . .	$C_2^2H_4^4O^2$	$11.50 = 8 \times 1.438$
{ Propionic acid. . . . .	$C_3^3H_6^6O_2^3$	$17.42 = 12 \times 1.452$
{ Propaldehyde . . . . .	$C_3^3H_6^6O^2$	$15.93 = 11 \times 1.448$
{ Butyric acid . . . . .	$C_4^4H_8^8O_2^3$	$22.01 = 15 \times 1.467$
{ Butaldehyde . . . . .	$C_4^4H_8^8O^2$	$20.52 = 14 \times 1.466$

(In the formula given above the upper figures represent the number of refraction steres, the lower the number of atoms in the compounds.)

In unsaturated compounds the doubly-bound carbon-atom has a refraction-stere twice as great as that of the singly-bound carbon-atom: thus ethyl crotonate,  $H_6^2H_{10}^6O_2^3$  has the same refraction equivalent as ethyl butyrate,  $C_6^6H_{12}^6O_2^3$ , or methyl valerate or amyl formate.

In the case of amylene, valerylene, and the allyl and propargyl compounds, the value of the refraction-equivalent is rather less, whilst in aromatic compounds the value is rather more than that required by this theory.

The refraction-stere of chlorine is  $Cl_4^4$ , or four times as great as that of hydrogen or carbon; the value varies slightly, according to whether it is combined with a carbon-, with or without a hydrogen-atom. Paraldehyde behaves as  $C_6^6H_{12}^6O_3^4$ , as containing one doubly-bound carbon-atom, and not as  $C_6^6H_{12}^6O_3^3$ . According to this theory, the formulæ which represent the refraction constitution of saturated compounds agree with the formulæ which represent their volume constitution; but for unsaturated compounds the volume- and refraction-stere vary in a different manner.

V. H. V.

**Optical Activity of Malic Acid and Malates at Different Temperatures.** By T. THOMSEN (*Ber.*, 15, 441–445).—Schneider (Abstr., 892, 1881) came to the conclusion that the rotatory power of malic acid and malates does not follow the author's law of multiple rotatory proportion. The author considers this conclusion unfounded; for in order to compare substances with one another, it is necessary to examine them under similar conditions, and therefore when the rotatory power of a substance varies differently with the concentration, the extremes only must be taken into consideration for the sake of comparison. But when substances vary with the temperature also, they cannot be compared directly with others, and cannot therefore be used to prove a general law. The author contends that malic acid and malates are such substances, and gives tables of the results of the examination of malic acid, and some malates of different concentration at different temperatures. To illustrate this he compares his own numbers with those calculated by Schneider's formulæ, and finds differences which vary considerably. The rotatory power of tartaric acid is also influenced by temperature, and hence anomalous results are obtained with that substance.

D. A. L.

**Photochemical Reaction of Ferric Oxalate.** By JODIN (*Compt. rend.*, 94, 1315–1316).—The photochemical sensitiveness of solutions

of ferric chloride mixed with oxalic acid varies with the composition of the mixture, and is greatest in dilute solutions, but is not strictly proportional to the degree of concentration of the solution. Apparently the sensitiveness diminishes somewhat more rapidly than the concentration of the solution increases. The presence of an excess of ferric salt greatly diminishes the sensitiveness, and the same effect is brought about by partial substitution of tartaric for oxalic acid. The mixture of ferric chloride and oxalic acid very readily absorbs certain rays in the spectrum, and the solution becomes heated  $5^{\circ}$  or  $6^{\circ}$  higher than solutions of uranium nitrate, potassium bichromate, or certain other ferric salts, of practically the same colour, when all the solutions are exposed to sunlight of the same intensity. C. H. B.

**Polarisation of Electrodes and Conductivity of Liquids.** By E. BOUTY (*Compt. rend.*, **94**, 1243—1247, and 1301—1304).—The author has applied Lippmann's method of determining the resistance of liquids to the measurement of the electromotive force of polarisation. With currents of feeble density\* between platinum electrodes in acidulated water, whatever the E.M.F. of the battery, the polarisation of both electrodes is at first too slight to be measured. It attains its limit at the negative electrode, where it is slight, after some minutes, and at the positive electrode, where it is considerable, after some hours. Determinations of the resistance of columns of liquid with E.M.F. varying from 0.365 to 11.76 volts, and intensity of current varying between the ratio of 1 to 32, show that *a liquid conducts electricity in one manner only, whatever the phenomena manifested at the electrodes*. This law also holds good for mixtures of electrolytes. From experiments with mixtures of solutions of copper salts with acidulated water or salts of more oxidisable metals, the author concludes that the conductivity of a mixed solution is always greater than that of any one of its constituents at the same degree of dilution. Hence it would appear that the molecules of each salt take part in the transmission of the electricity, though only one of the salts is decomposed. The polarisation of the positive electrode may generally be neglected. The polarisation of the negative electrode is very slight for currents of low density, but increases rapidly below or above that particular density at which a brown deposit is formed. The polarisation is accompanied by development of heat, due to local action between the metal deposited and the other salt which is not decomposed. *The electrolytic reaction which takes place at the electrodes with currents of low density always absorbs less heat than that which succeeds it with currents of higher density*. According to Wiedemann, in a solution containing salts of any two of the following metals, zinc, cadmium, lead, copper, silver, gold, that which comes later in the list is deposited to the exclusion of that which precedes it. The author finds that the electrolysis of the first salt takes place in its turn when the density of the current is sufficiently high. This order of the metals is the same as that of the heats of formation of their salts, those of zinc salts being the highest, and those of the gold salts the lowest. C. H. B.

\* By the term *density* is understood the intensity of the current for unit-surface of the electrode.

**Effects Produced in a Vacuum by the Current from a Gramme Machine.** By JAMIN and G. MANEUVRIER (*Compt. rend.*, **94**, 1271—1273).—The phenomena observed on passing the current from a Gramme machine between carbon points in a vacuum produced by an air-pump, are similar to those observed with induced currents in Geissler tubes, but are much more brilliant. Single carbon pencils become red hot, and the vessel is filled with a blue gas, which deepens in colour. Eventually the walls of the vessel are covered with a finely divided black powder, which dissolves in nitric acid with effervescence and incandescence. Whether it is pure carbon or a compound of carbon and hydrogen has not yet been ascertained. If instead of single carbon pencils conical bundles of several smaller pencils are employed, the carbons become much less heated, and volatilisation is almost prevented.

With bundles of copper wires 3 mm. diameter, the effects are still more brilliant. If the current is very intense, the wires are melted, and in all cases copper is volatilised and deposited on the sides of the vessel.

C. H. B.

**Depression of the Zero Point in Mercurial Thermometers.** By J. M. CRAFTS (*Compt. rend.*, **94**, 1298—1301).—It is well known that on heating a thermometer which has remained at ordinary temperatures for a long time, the zero point is lowered by an amount which, between  $0^{\circ}$  and  $100^{\circ}$ , is proportional, as Pernet has shown, to the square of the temperature. For higher temperatures Mills found a different order of things, but his results were apparently obtained with thermometers which had not been subjected to proper preliminary treatment. Before measuring the depression of zero caused by heating, it is necessary to be certain (1) that at starting the zero is at its maximum position, and (2) that the depression is not masked by a permanent rise of the zero, which always takes place on heating, even for a few minutes, a thermometer which has not for a long time been heated to the particular temperature of the experiment. This permanent rise can be prevented by suitable preliminary treatment. A thermometer so prepared is heated to  $355^{\circ}$ , and the zero point taken on cooling. It is then subjected to any series of operations, again heated to  $355^{\circ}$ , and the zero point again observed. It is found to occupy the same position as after the first heating. The depression of zero caused by boiling the mercury in a thermometer is about  $2^{\circ}$  for French lead glass. The rise after six months at ordinary temperatures is from  $0.4^{\circ}$  to  $0.5^{\circ}$ ; the subsequent rise during five or ten years rarely exceeds  $0.5^{\circ}$ , and after ten years the zero remains constant. After depression caused by heating, the zero point can, however, again be raised to its original position by prolonged heating at a somewhat lower temperature, but the greater the interval between the temperature which causes the depression and that to which the thermometer is heated in order to raise the zero point, the slower is the rise of the zero; and if the interval is greater than  $100^{\circ}$ , the rise is probably never complete.

In order to get rid of the abnormal tension produced by blowing the glass, thermometers 1 and 5 were heated 11 days at  $355^{\circ}$ ; 13 and 15, for three years at  $206^{\circ}$  and  $266^{\circ}$ ; 31 and 32, before being filled

with mercury, were heated for 100 hours at  $440^{\circ}$ , and then cooled gradually for 100 hours; finally, all six were heated for a day at  $306^{\circ}$ , and the zero points observed. In order to raise the zero from the point to which it had been lowered by heating at  $306^{\circ}$ , all the thermometers were heated 4 days at  $218^{\circ}$ , 18 days at  $100^{\circ}$ , 5 days at  $80^{\circ}$ , 7 days at  $60^{\circ}$ , 6 days at  $40^{\circ}$ , 9 days at  $20^{\circ}$ , 3 days at  $10^{\circ}$ , and 2 days at  $0^{\circ}$ . The following table gives the depression of zero caused by heating to the temperature placed at the head of the column:—

		$40^{\circ}$ .	$60^{\circ}$ .	$80^{\circ}$ .	$100^{\circ}$ .	$160^{\circ}$ .	$218^{\circ}$ .	$260^{\circ}$ .	$306^{\circ}$ .	$355^{\circ}$ .
Therm.	1 ....	—	0.06	0.19	0.31	0.74	1.12	1.33	1.63	2.19
	5 ....	0.04	0.08	0.18	0.29	0.56	0.76	0.91	1.14	1.51
	13 ....	0.02	0.03	0.17	0.31	0.69	0.87	1.09	1.30	2.15
	15 ....	0.01	0.05	0.18	0.31	0.75	0.97	1.12	1.40	2.05
	31 ....	0.02	0.06	0.22	0.37	0.84	1.15	1.46	1.77	—
	32 ....	—	—	—	0.28	0.69	0.98	1.21	1.56	2.06

With the exception of No. 5, which was made of German soda glass, the numbers given are so close that they may, without sensible error, be used for correcting thermometers of French lead glass for the depression of zero caused by heating.

C. H. B.

**Apparatus for Determination of the Melting Points of Easily Fusible Metals and Alloys.** By L. LIEBERMANN (*Ber.*, 15, 435—437).—In the apparatus described, the metal to be examined is supported in an oil-bath, between two horizontal graphite plates, which in their turn are kept in position by means of two stout platinum wires, fixed in two porcelain tubes passing through a cork; through another hole in the cork a thermometer is fixed and dips into the bath. In using the apparatus, an electric current is passed through the platinum wire, the circuit being completed by the alloy, so that a bell rings continually as long as the current is closed; the bath is now heated, and as soon as the metal melts, the circuit is broken and the ringing ceases; at this point the thermometer is read. The means of the melting point of a sample of tin are, in oil-bath,  $227.8^{\circ}$ ; in  $\text{CO}_2$ ,  $228.4^{\circ}$ ; in air,  $228.2^{\circ}$ ; and of a tin alloy in oil,  $98^{\circ}$ ; in  $\text{CO}_2$ ,  $95^{\circ}$ . A woodcut of the apparatus is given.

D. A. L.

**Use of Liquid Ethylene for producing Low Temperatures.** By L. CAILLETET (*Compt. rend.*, 94, 1224—1226).—Ethylene liquefies under a pressure of 63 atmos. at  $+10^{\circ}$ , 56 atmos. at  $8^{\circ}$ , 50 atmos. at  $4^{\circ}$ , and 45 atmos. at  $1^{\circ}$ . Its critical point is about  $13^{\circ}$ . The temperature of the liquid at ordinary pressure is approximately  $-105^{\circ}$ , much lower than that of nitrous oxide. Moreover, ethylene remains liquid and transparent at temperatures at which nitrous oxide and carbonic anhydride are solid and opaque. If a jet of the liquid is allowed to play on the apparatus to be cooled, a very low temperature is obtained, and a quantity of the liquid can be recovered. When oxygen is highly compressed in a capillary tube, cooled by this method below  $-105^{\circ}$ ,

and the pressure is suddenly released, a violent ebullition is observed at a certain distance from the bottom of the tube; but the author has not yet been able to determine whether this liquid exists before the pressure is released, or is produced by the sudden expansion.

C. H. B.

**The Critical Temperature of Liquids.** By B. PAWLEWSKI (*Ber.*, 15, 460—462).—The author's experiments lead him to the following conclusions:—

1. The critical temperature ( $T$ ) of homologous compounds differs from the boiling point ( $t$ ) by a constant difference, and can therefore be represented by the formula  $T = t + \text{constant}$ .

2. Isomeric ethers have identical, or at least very similar, critical temperatures. With other isomeric compounds, however, this is not the case, as is evident from the above statement.

3. Bodies containing double carbon-bonds have higher critical points than those which do not contain this sort of combination, agreeing with the behaviour of such isomerides as regards their boiling points.

4. The critical temperature ( $T_m$ ) of a mixture of two liquids is thus formulated:—

$$T_m = \frac{nT + (100 - n)T'}{100} \quad (I),$$

$n$  and  $100 - n$  being the percentage of each liquid present;  $T$  and  $T'$  the respective critical temperatures of the liquids.

5. The critical point of the mixture having been found by formula (I) and its percentage composition and the critical point of the low-boiling constituent ( $T$ ) being known, the critical point of the high-boiling constituent ( $T'$ ) is thus obtained:—

$$T' = \frac{100 T_m - nT}{100 - n}.$$

6. If, on the other hand, the critical temperatures of the mixture and of the two constituents are known, the percentage composition of the liquid mixture can be calculated as follows for one of the constituents in formula I:—

$$n = 100 \left( \frac{T_m - T'}{T - T'} \right).$$

Mixtures of several bodies behave in an exactly similar manner to those of two bodies. The author suggests that the constitution of mixtures of liquids can be determined by this process with as great a facility and accuracy as with the polariscope.

The critical points of liquids which dissolve glass at high temperatures, *e.g.*, water, cannot be determined by this process.

D. A. L.

**Thermochemistry of Ozone.** By F. MULDER and H. G. L. VAN DER MEULEN (*Ber.*, 15, 511—513).—Berthelot has obtained 131,600 cal. as the mean, and 137,600 cal. as the maximum value for the expression  $As_2O_3Aq$  3000. The authors have modified Berthelot's process thus:—1. The ozonised oxygen is led from the generator



through a glass gasometer filled with water, and thence into the calorimetric flask. 2. The end of the delivery tube in the flask is filled with capillary tubes. 3. The exit tube from the calorimetric flask is connected with an aspirator. 4. The arsenious acid is dissolved in water without hydrochloric acid. 5. It was titrated with a solution of iodine in potassium iodide solution. The results of two experiments give as mean 143,300 cals., the maximum being 145,000 cals. for the above expression. Hence for 00 00 00 the authors have the mean  $-64,820$  cals. against Berthelot's  $-53,320$  cals.

D. A. L.

**Heats of Combustion of Hydrocarbons.** By D. MENDELEJEFF (*Jour. Russ. Chem. Soc.*, 1882, 230—238).—The thermochemical data referring to the heat of combustion are, according to the author, mostly direct calorimetric data, from which the influence of physical and chemical changes which accompany chemical reactions has not been sufficiently eliminated, and yet it is necessary to separate the heat of reaction itself from the heat which is due to physico-mechanical phenomena, in order to determine the relation between heat and chemical changes. This refers especially to the carbon compounds, as from their heat of combustion conclusions are drawn as to their formation from the elements, and yet the heat of formation of carbon compounds is very small, compared with the total heat of combustion. The difference arising therefrom is seen from the following example:—

The reactions which take place when either carbon dioxide or water acts on glowing charcoal, are analogous not only as regards the volume, but also in chemical and technical, and even in thermal respects, if the physical phenomenon which accompanies the second reaction is not taken into account. In the first reaction, viz.,  $\text{CO}_2 + \text{C} = \text{CO} + \text{CO}$ , 39·8 T.U.\* are absorbed, this being the difference between the heat of combustion of 1 atom of carbon = 97 T.U. and the combustion of  $\text{CO} = 68·4$  T.U. ( $97·0 - 2 \times 68·4 = -39·8$  T.U.). The second reaction, viz.,  $\text{H}_2\text{O} + \text{C} = \text{CO} + \text{H}_2$ , is accompanied by a heat phenomenon of  $-39·8$  T.U., which is the difference of  $97·0 - 2 \times 68·4$ , 68·4 being the heat of combustion of  $\text{H}_2 + \text{O}$ . In both cases an equal absorption of 39·8 T.U. takes place. If the combustion of hydrogen in the calorimeter could take place with formation of aqueous vapour only, it might be concluded, that the combustion of the molecules  $\text{CO}$  and  $\text{H}_2$  is accompanied by an identical evolution of heat, and further, from the above two reactions, the conclusion might be drawn, that on combustion of 1 atom of carbon in the gaseous state  $2 \times 68·4 = 137$  T.U. are evolved. This last conclusion has been already arrived at by Rankine, who supposed that both states of the combustion of carbon, viz., its combustion into  $\text{CO}$  and the conversion of the latter into  $\text{CO}_2$ , are accompanied by the evolution of the same quantity of heat. Assuming this, we are led to the very probable conclusion, that the formation of all hydrocarbons is without exception an *exothermic* reaction and not partly an *endothermic* one, as is generally assumed, for example by Thomsen and Berthelot. It is, *e.g.*, very improbable that the formation of acetylene, the only hydrocarbon which is formed from carbon and hydrogen directly, would be accom-

\* T.U. stands for "large" or kilogram-degree thermal units.

panied by an absorption of heat, equal to  $-61$  T.U., according to Berthelot, or to  $-48$  T.U. according to Thomsen. Assuming that the heat of combustion of 1 atom of carbon in the hypothetical gaseous state, is  $= 137$  T.U., the heat of formation of acetylene will be  $+ 25$  T.U. (from Berthelot's data) or  $+ 32$  T.U. (from Thomsen's data). The author further remarks, that in the conclusions with regard to the heat of formation of hydrocarbons from hydrogen and charcoal (Thomsen), or hydrogen and diamond (Berthelot), the evolution or absorption of heat which accompanies the reaction, and is due to physical and mechanical processes, is not accounted for, and that the conclusions refer to entirely illusory reactions. If the direct formation from C and H could really take place, the reaction would have to be represented in a manner totally different from what it is at present, because all that we know about diamond or charcoal leads to the assumption that the molecule is a very complicated one, or that it contains  $C_n$ ,  $n$  being a large number.\* The author thinks that a comparative study of the heat of combustion of carbon and carbon-compounds, may lead to the solution of the question as regards the complicated nature and the constitution of the carbon molecule and not *vice versa*, as we know about the constitution of hydrocarbons far more than about the molecular constitution of carbon itself. All we know about the heat of formation of hydrocarbons from carbon and hydrogen shows, that the reaction takes place with only a small development or absorption of heat, which is often less than 1 per cent. of the whole heat of combustion itself, whereas for the heat of combustion of one and the same hydrocarbon, numbers are given by different observers, showing differences of several per cent., so that all the conclusions with regard to the constitution of hydrocarbons which were drawn from their heat of combustion, cannot be regarded as certain, even from the experimental point of view. The conclusions lately arrived at by Thomsen on the relation between constitution and heat of formation are regarded by Mendelejeff as insufficient, because Thomsen starts from the heat of formation of four hydrocarbons ( $CH_4$ ,  $C_2H_4$ ,  $C_2H_6$  and  $C_3H_2$ ), and arrives at five conclusions at least (namely, as regards the heat of dissociation of carbon, the mode of linking between carbon and hydrogen, and finally, the heat of mutual combination of carbon-atoms by means of one, two, and three "bonds of affinity.") This explains why the conclusions arrived at by Thomsen as to the structure of benzene, are really in contradiction with his own theory. Mendelejeff shows that, whereas according to Thomsen's recent experiments, the heat of formation of benzene is  $= -2.27$  T.U., Ladenburg's formula for benzene, with nine single linkings between the carbon-atoms, would require, according to Thomsen's theory, a number  $= -14.85$  T.U. Although the experimental number ( $-2.27$  T.U.) does not agree with Thomsen's theory ( $-14.85$  T.U.), yet the difference between the experimental number and the number calculated for Kekulé's formula, is still greater, as that formula (for three single and three double linkings) would require

\* Important reasons for such an assumption were given by Mendelejeff in 1870, in his most interesting paper (published in the same Journal in 1870), "On the Law of Specific Heat, and the Composition of the Carbon Molecule."—B. B.

— 58.56 T.U. for the heat of formation of benzene. The same can be said as regards the data obtained by Thomsen for dipropargyl. From all this Mendelejeff concludes, that our knowledge as regards the relation between the heat of combustion of hydrocarbons and their constitution cannot be considered satisfactory.

In the gaseous state alone can the thermal relations be regarded as being free from the influence of the change of the internal work, and it is therefore necessary for comparison to refer the thermal values to the gaseous state. In order to refer the heat of combustion of solids or liquids to the gaseous state, it is evident that the latent heat of fusion and evaporation of the bodies in question, must be added to the values found by experiment, and the heat of evaporation of water subtracted from them; for water (1 mol. in grams) the last value is = 10.7 T.U. between 15—20°; but the heat of evaporation of hydrocarbons and other combustible bodies is only very little known, although in the majority of cases it lies between 4—10 T.U. for the gram-molecule. It further appears that in the case of homologous bodies the heat of evaporation increases with increasing molecular weight and boiling point, but in this direction especially further investigations are needed. But as the heats of combustion are not yet quite exactly determined, and the heat of evaporation is small compared with the heat of combustion, Mendelejeff proposes to apply for the heat of evaporation of bodies for which this value cannot be, or has not yet been determined directly, an approximate correction which falls within the limits of the experimental errors. For heptane the author assumes the heat of evaporation to be = 7 T.U. (always for 1 mol. in grams), and for naphthalene and anthracene he assumes the sum of the heat of fusion and evaporation to be = 15 T.U., whereas their heat of combustion is over 1000 T.U.

Another correction must be introduced for the quantity of heat which is set free or absorbed when mechanical work is carried on, owing to the expansion or condensation which takes place when the volume of gas before and after combustion is not the same. As the volume of every molecule is the same in the state of vapour, and the molecule (2 grams) of hydrogen occupies a volume of 23.86 litres, at the pressure of 760 mm., and at the temperature of 19°, which is the temperature of most of Thomsen's experiments, a contraction corresponding to this volume will be, at the above pressure, equal to the pressure of 1033 grams for 1 square cm. or  $1033 \times 23,860 = 246.5$  kilogram-meters. On dividing this value by the mechanical equivalent of heat,  $\frac{246.5}{430}$ , the quantity of heat absorbed in the above contraction in large thermal units, is found. It is = 0.57 T.U. Consequently, whenever a contraction corresponding to 1 mol. or to two volumes takes place, 0.57 T.U. must be subtracted from the experimental number given in large thermal units, or added when a corresponding expansion takes place. In the last column of the first table below, numbers are given for the heat of combustion of a series of hydrocarbons after the application of a correction for the contraction or expansion, for the change from the solid or liquid into the gaseous state, and for other physical processes taking place at the same time.

Name of compounds.	Molecular position of the compound burnt.	Molecular weight of the compound.	Number of atoms or volumic mols. of oxygen needed for the combustion of 1 mol. (2 vols.).	Number of divolumic mols. of the product of combustion $\text{CO}_2 + \text{H}_2\text{O}$ .	Calorimetric data for the compounds in the solid, liquid, or gaseous state. $\text{CO}_2$ as gas, $\text{H}_2\text{O}$ liquid. Large thermal units.*	Heats of combustion calculated for the compound and for water in the gaseous state.†	Total volume of the compound before the combustion, $\text{H} = 1$ .	Volume of the products of combustion, $\text{H} = 1$ .	Heat of combustion, with correction for the mean chemical work.
1. Hydrogen .....	$\text{H}_2$	2	1	0 + 1	gas 68.4 T.	57.7	3	2	57.4
2. Methane .....	$\text{CH}_4$	16	4	1 + 2	gas 213.5 B.	192.1	6	6	192.0
3. Ethane .....	$\text{C}_2\text{H}_6$	30	7	2 + 3	gas 373.5 T.	341.2	9	10	342.0
4. Propane .....	$\text{C}_3\text{H}_8$	44	10	3 + 4	gas 533.5 T.	490.7	12	14	492.0
5. Heptane (b. p. 99°) ..	$\text{C}_7\text{H}_{16}$	100	22	7 + 8	liq. 1137.4 L.	1058.8?	24	30	1062.0
6. Ethylene .....	$\text{C}_2\text{H}_4$	28	6	2 + 2	gas 334.8 T.	313.4	8	8	313.0
7. Propylene .....	$\text{C}_3\text{H}_6$	42	9	3 + 3	gas 495.2 T.	463.4	11	12	464.0
8. Amylene .....	$\text{C}_5\text{H}_{10}$	70	15	5 + 5	liq. 804.4 F. & S.	756.2	17	20	758.0
9. Pentylene (b. p. 107°) ..	$\text{C}_5\text{H}_{12}$	98	21	7 + 7	liq. 1095.0 L.	1027.1?	23	28	1030.0
10. Cetene .....	$\text{C}_{16}\text{H}_{32}$	224	48	16 + 16	liq. 2476.3 F. & S.	2313.1?	50	64	2320.0
11. Acetylene .....	$\text{C}_2\text{H}_2$	26	5	2 + 1	gas 310.4 T.	299.7	7	6	299.0
12. Allylene .....	$\text{C}_3\text{H}_4$	40	8	3 + 2	gas 466.5 B.	445.1	10	10	445.0
13. Turpentine .....	$\text{C}_{10}\text{H}_{16}$	136	28	10 + 8	liq. 1475.9 F. & S.	1399.7	30	36	1403.0
14. Dipropargyl .....	$\text{C}_6\text{H}_6$	78	15	6 + 3	gas 883.2 T.	851.1	17	18	852.0
15. Benzene .....	$\text{C}_6\text{H}_6$	78	15	6 + 3	gas 788.0 T.	755.9	17	18	756.0
16. Naphthalene .....	$\text{C}_{10}\text{H}_8$	128	24	10 + 4	sol. 1258.4 R.	1230.6	26	28	1232.0
17. Anthracene .....	$\text{C}_{14}\text{H}_{10}$	178	33	14 + 5	sol. 1775.9 R.	1737.4	35	38	1739.0
18. Wood charcoal .....	$\text{C}^*$	$x \cdot 12$	$x \cdot 2$	$x + 0$	sol. $x \cdot 97 \cdot 0$ F. & S.	?	$2 + 2x$	$2 \cdot x$	?
19. Diamond .....	$\text{C}_y$	$y \cdot 12$	$y \cdot 2$	$y + 0$	sol. $y \cdot 94 \cdot 5$ F. & S.	?	$2 + 2y$	$2 \cdot y$	?
20. Carbon monoxide ....	$\text{CO}$	28	1	1 + 0	sol. 68.4 T.	68.4	3	2	68.1

\* F. &amp; S. = Favre and Silbermann, B. = Berthelot, T. = Thomsen, L. = Louguine, R. = Rechenberg (1880).

† Heats of combustion of compounds in the solid or liquid state, the heats of fusion or of evaporation of which have not yet been determined, are marked with a sign of interrogation.

From the first table the values of the second have been calculated, the last column of the former being identical with the first column of the latter. This table contains the heats of formation of hydrocarbons from methane, carbon monoxide and carbon dioxide, which values, according to Mendeleeff, are of more real interest than the heats of formation from carbon and hydrogen, as transformations of the above kind really and often occur. In all the values corrections of the above nature are introduced. If the heat of combustion of a hydrocarbon  $C_nH_{2m}$  be T, its heat of formation from methane will be:—

$$nCH_4 - (2n - m)H_2 = 77.8n + 56.8m + 0.57 - T,$$

from CO—

$$nCO + (n + m)(H_2 - nH_2O) = 124.9n + 55.8m + 0.57 - T,$$

and from  $CO_2$ —

$$nCO_2 + (m + 2n)H_2 - 2nH_2O = 114.2n + 56.8m + 0.57 - T.$$

	Heat of combustion.	Heat of formation from		
		CH <sub>4</sub> .	CO.	CO <sub>2</sub> .
	T. U.	T. U.	T. U.	T. U.
CH <sub>4</sub> .....	192	—	+ 47	+ 36
C <sub>2</sub> H <sub>6</sub> .....	342	— 15	+ 79	+ 58
C <sub>3</sub> H <sub>8</sub> .....	491	— 30	+ 111	+ 79
C <sub>7</sub> H <sub>16</sub> .....	1061	— 61	+ 268	+ 143
C <sub>2</sub> H <sub>4</sub> .....	313	— 43	+ 51	+ 30
C <sub>3</sub> H <sub>6</sub> .....	464	— 60	+ 82	+ 50
C <sub>5</sub> H <sub>10</sub> .....	757	— 83	+ 152	+ 98
C <sub>7</sub> H <sub>14</sub> .....	1029	— 86	+ 243	+ 168
C <sub>16</sub> H <sub>32</sub> .....	2317	— 163	+ 582	+ 411
C <sub>2</sub> H <sub>2</sub> .....	299	— 86	+ 8	— 13
C <sub>3</sub> H <sub>6</sub> .....	415	— 97	+ 44	+ 12
C <sub>10</sub> H <sub>16</sub> .....	1401	— 168	+ 303	+ 196
C <sub>6</sub> H <sub>6</sub> (Dip.) .....	851	— 213	+ 69	+ 5
C <sub>6</sub> H <sub>6</sub> (Benz.) .....	756	— 118	+ 174	+ 110
C <sub>10</sub> H <sub>8</sub> .....	1231	— 125	+ 246	+ 139
C <sub>14</sub> H <sub>10</sub> .....	1738	— 364	+ 295	+ 145

B. B.

**Danger of Gas Explosions.** By MALLARD (*Chem. Centr.*, 1882, 268).—A series of experiments was made with a view of ascertaining the rate at which the ignition in explosive mixtures travels. The following measurements of velocity were obtained:—

Vol. of marsh-gas per vol. of air.	Velocity of ignition per second.	Vol. of common gas per vol. of air.	Velocity of ignition per second.
	m.		m.
0·086	0·041	0·150	0·285
0·103	0·325	0·166	0·617
0·115	0·505	0·180	0·820
0·120	0·550	0·190	0·985
0·127	0·524	0·200	1·010
0·130	0·515	0·210	0·935
0·134	0·440	0·230	0·740
0·140	0·375	0·300	0·097
0·161	0·139	—	—

It is shown that mixtures containing less than 0·117 gas per litre of air are no longer explosive, and cease to be inflammable *per se*. By taking a burner consuming 140 litres of gas per hour fitted to a pipe 6 mm. in diameter, the gas will pass through the pipe at a velocity of 1·4 m. per second. At the opening of the burner the velocity of the current is considerably more, probably 10 m.; however, the rate at which the most explosive gaseous mixture can travel is only 1 m., hence there cannot be any danger of the flame travelling back into the pipe.

D. B.

**Formation of Alloys by Pressure.** By W. SPRING (*Ber.*, 15, 595—597).—In continuation of his former investigations (this Journal, 40, 498; 42, 273) the author concludes that *matter assumes that condition which corresponds to the volume which it is made to occupy*. This statement is confirmed by the formation of alloys from their constituent elements by the action of great pressure. Thus, a mixture of filings of bismuth, cadmium, and tin in the proportion necessary to form Woods' alloy, on being subjected to a pressure of 7,500 atmospheres, gave a metallic block which resembled Woods' metal in all its properties, such as density, colour, hardness, and brittleness, and melted under water at 70° (Woods' metal melts at 65°). Rose's alloy (m. p. 95°) was obtained in a similar manner from lead, bismuth, and tin. Ordinary brass was likewise produced by repeatedly subjecting a mixture of zinc and copper filings to great pressure. The fact that the sp. gr. of brass is nearly the same as that of both the constituent metals, explains why the alloy is not easily produced by pressure, and is therefore a further confirmation of the author's theory. Romna has also found that a fine platinum wire covered galvanically with a coating of silver, after passing through a wire-drawing plate, is completely soluble in nitric acid. This is evidently due to the two metals having been alloyed by the pressure in passing through the plate.

T. C.

**Influence of one Metal on the Surface of another Metal placed at a Short Distance.** By H. PELLET (*Compt. rend.*, 94, 1247—1249).—If two metallic surfaces are placed parallel to one another at a distance of a few millimeters or tenths of a millimeter,

the properties of the superficial layer of each surface undergo a slight alteration, due to the proximity of the other metal, and depending on the nature of the latter. This change is produced slowly, and at first increases with the time, but afterwards tends to a limit. It is not permanent, for, if the influencing metal is removed, the metal influenced gradually assumes its original condition. The amount of change was measured by comparing the difference of potential between a gilded brass surface and that of the particular metal before and after the latter had been subjected to the influence of a second metal. Of the metals used lead and iron produced the greatest effect, but the change was very distinct with copper, platinum, and gold. Zinc appears to cause no change in the surface of copper, gold, or zinc. The phenomenon is not purely electrical, but is of a material character. It is probably similar to the phenomenon of Moser's figures, and is possibly related to the fact that many metals have a slight but distinct odour. The influence of copper on zinc is perceptible, even when their surfaces are 10 mm. apart. It would appear as if the metals give off at the ordinary temperature a volatile substance which can be deposited on other bodies, producing chemical change. When the influencing body is removed, the volatile substance gradually leaves the influenced surface, which resumes its original condition.

C. H. B.

**Remarks on the Atomic Weights.** By A. BUTLEROFF (*Journ. Russ. Chem. Soc.*, 1882, 208—212).—Referring to Schützenberger's latest experiments, who pretends to have obtained in analysing certain hydrocarbons, either a normal result or a sum exceeding 100, according to circumstances, the author attempts to explain this anomaly, assuming that Schützenberger's experiments do not include an error, by one of the following three hypotheses:—

(1.) The excess of matter might be explained by the conversion of force (energy) into matter.

(2.) The absolute quantity of matter remained unaltered, but its increase in weight is due to the circumstance that its attraction by the earth has increased in the meantime. Both these assumptions are, however, not very probable.

(3.) The anomaly is due, not to a change in weight, but to a change in the chemical significance or value. The author assumes that the atomic weight, that of carbon, for example, may vary within narrow limits, *e.g.*, between 11·8—12; and, in order to settle this question, he has undertaken some experiments especially to determine the atomic weight of white and red phosphorus under otherwise equal circumstances, and further to synthesise mercuric chloride from a known weight of the metal and from chlorine, either in its usual state, or after insolation by sunlight, or after the action of electricity, &c. By this hypothetical variation of the atomic weights, the author explains the fact that the atomic weights of elements are not exactly, but *very nearly*, whole multiples of that of hydrogen. This is hardly due to mere chance, as Marignac remarked more than twenty years ago (1860), and as Mallet and F. W. Clarke have pointed out again recently, so that Prout's hypothesis is not to be regarded as being without real foundation. According to Marignac, the numerical data obtained

by experiment, may only approach "Prout's law," as is the case with Boyle's law, and the author asks whether Prout's hypothesis might not, like Boyle's law under certain circumstances, be rigidly accurate. As there is no reason *à priori* to assume a constancy of atomic weights, the atomic weight would represent for the chemist a quantity of matter which is a carrier of a known quantity of chemical energy varying within *narrow* limits. The author has no reason to regard the above suppositions as entirely impossible, and will therefore proceed in his experiments.

B. B.

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## Inorganic Chemistry.

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**Liquefaction of Ozone.** By P. HAUTEFEUILLE and J. CHAPPEIS (*Compt. rend.*, **94**, 1249—1251).—The authors have made further experiments on the liquefaction of ozone with the aid of the apparatus used by Cailletet for the liquefaction of ethylene, and have obtained a deep indigo-blue liquid which can be preserved more than thirty minutes under a pressure of 75 atmos. and evaporates somewhat slowly at ordinary pressures. A mixture of oxygen and ozone was compressed at 125 atmospheres in the pressure tube of Cailletet's apparatus, the capillary tube being curved and the lower end cooled by a jet of liquid ethylene. If the mixture used does not contain more than 10 per cent. of ozone by weight, the gas under 125 atmos. pressure is not sensibly coloured in the main part of the tube, but the blue colour is very distinct in the cooled part of the capillary tube. Whether this coloration is due to a liquid mixture of ozone and oxygen, or to a thin film of liquid ozone alone, could not be definitely decided. Sudden release of pressure produces no cloudiness. The tube, however, instantly becomes colourless, whilst a drop of a deep indigo-blue liquid (ozone) remains in the end of the capillary tube, and evaporates very slowly. That the ozone is almost entirely liquefied is shown by the fact that on again compressing the gas to 150 atmos. no further coloration is produced. Although the ozone evaporates slowly it diffuses somewhat rapidly. The gas above the almost black liquid is quite colourless, and it is only just when the last traces of the liquid disappear that the gas is seen to have a blue colour.  
C. H. B.

**Chlorination of Sea-Water.** By B. DE LA GRYE (*Ann. Chim. Phys.* [5], **25**, 433—477).—This paper contains the results of an elaborate series of determinations of the amount of chlorine in sea-water made during a voyage round the world, 1874—1875 (expedition to Campbell Island). The chlorine was determined volumetrically by silver nitrate with potassium chromate as indicator, and tables are given showing the rates of expansion of the pipettes and standard solutions employed. Extensive tables are given showing the quantity of chlo-

rine per litre of sea-water at different points in the Mediterranean, Suez Canal, Red Sea, Indian Ocean, Pacific, and Atlantic. The average amount is about 20 grams per litre, but this varies considerably in different localities, and is materially affected by the distance from the shore, especially if the land is watered by large rivers. The minimum, 17.5 grams per litre, was found to the north of Batavia; here the sea was quite muddy from the solid matter washed from the surrounding islands by the rivers, which were then in flood owing to the heavy rains. The maximum in the sea (omitting the Suez Canal) was 22.36 grams per litre, found in the Red Sea 30 miles S.S.E. of Jubbal. In some parts of the Mediterranean the chlorine is as high as 22 grams per litre, and increases distinctly from west to east. Approaching Egypt, however, the influence of the fresh water of the Nile is perceptible before the land is visible. The amount of chlorine diminishes rapidly by 0.8 gram per litre, while the thermometer and densimeter show no variation. At Port Said the amount is still lower. In the north part of the Suez Canal the influence of the fresh water from the Nile and other sources is very marked. The quantity of chlorine begins, however, to increase at the second station, and increases slowly up to El Kantara, then rapidly as the Bitter Lakes are approached. At the latter point the amount of chlorine is as high as 37.2—37.47 grams per litre. This number differs from that found by Durand-Claye in 1872, the difference being due to the gradual solution of the banks of salt which form the bottom of these lakes, and to the entrance of sea-water during high tides. The determinations quoted were made just two hours after high water. In the Red Sea the amount of chlorine diminishes from north to south. At first it is a little higher than in the Mediterranean, but rapidly falls below owing to the influence of the heavy rains which accompany the monsoons. Determinations made in the Pacific confirm the law that the salinity of sea-water is higher under the tropics than under the equator and beyond the tropics. Apparently it is higher under the south tropic than under the north, but this is possibly dependent on the season.

The author has determined the rate of expansion between  $0^{\circ}$  and  $30^{\circ}$  of sea-water containing amounts of chlorine varying from 0 to 34 grams per litre, and a table is given containing his results. The direct determination of the density of sea-water on board ship is a matter of considerable difficulty, and is affected by several sources of error. It may with advantage be replaced by a determination of the amount of chlorine. Comparison of the density determined by the densimeter with that deduced from the quantity of chlorine present leads to the following empirical rule for calculating the density from the amount of chlorine found when the latter does not much exceed 22 grams per litre:—*Multiply the amount of chlorine in grams per litre by 16, add the product, regarded as decimals of the fourth order, to 0.9944, and the result will be the density required.* The numbers calculated in this way agree very closely with those obtained by actual determination. The author considers that the determination of the amount of chlorine may with advantage be applied to the investigation of currents, determination of the distance from the shore at which the effect of large rivers such as the Amazon is perceptible, and similar problems. He

also discusses the effect upon the sea level of variations in density due to variations in the amount of chlorine. C. H. B.

**Formation of Hypochlorites and Chlorates from Chlorides by the Action of the Electric Current.** By A. LIDOFF and W. TICHOMIROFF (*Jour. Russ. Chem. Soc.*, 1882, 212—219).—The decomposition of solutions of halogen salts of alkali-metals under the influence of the voltaic current has been studied since 1851 by Watt, who proposed to prepare chlorine and hydrogen by the electrolysis of a solution of potassium chloride acidulated by sulphuric acid. In order to accelerate the reaction, different salts were added by Dixon in 1862. In 1872 Fitzgerald and Molloy used for the same purpose carbon electrodes, which were previously dipped into paraffin. In 1879 Gluchoff and Waschtschuk applied the chlorine evolved in this process for the formation of a gas battery which would strengthen the action of the main current. The last experiments in this direction were made by Kozloffsky and Lazareff in 1880 and 1881. In all the above experiments the alkaline residue was worked up for soda crystals or sodium hydrate, the chlorine for bleaching powder or alkaline hypochlorite.

The authors investigated the action of the silent discharge or of the voltaic current between carbon electrodes, generated by a Gramme engine, upon solutions of the chlorides of sodium, potassium, and calcium. As the chlorine evolved in this process is extremely active, it was improbable that it would escape in large quantities from the liquid. The ordinary voltaic current was replaced by the silent discharge as soon as the liquid began to get warmer. The evolution of chlorine, which was somewhat energetic in the beginning of the experiment, ceased almost entirely after a short time. On using sodium or potassium chloride, the liquid contained, besides chlorine, salts of hypochlorous acid, as was proved by many reactions, and of chloric acid, which was detected after the complete destruction of the hypochlorite by boiling or addition of ammonia, which according to Kolb, destroys hypochlorites on application of a moderate heat. Some of the potassium chlorate thus formed could even be separated in crystals.

The formation of bleaching liquor from a solution of calcium chloride went on much more slowly than in the case of chlorides of alkali metals, partly owing to the greater resistance in the interior of the liquid. The best yield is obtained from a neutral solution at a temperature of 60°; from an acid solution much free chlorine was evolved.

In order to study the further effect of the current on hypochlorites, which are formed in the above reaction, two litres of a solution of bleaching powder containing 8.25 grams of available chlorine in 100 c.c. were electrolysed. After two hours this amount diminished to 8.07 grams, and after two hours more to 7.75 grams, so that the total percentage loss of the amount of active chlorine was 6.06. The destructive action of the current on hypochlorites is therefore but very small. Though a rapid evolution of gas had taken place during the above experiments (about 6 litres were collected) the quantity of chlorine contained in them, or in the wash-water, was very small, not exceeding a few milligrams.

The authors explain the formation of hypochlorites in the above cases by the action of nascent chlorine on the alkalis, which are formed from the metals separated at first, by their immediate contact with water. They further assume that the chlorates are formed from the hypochlorites by the action of heat thus:  $3\text{MClO} = \text{MClO}_3 + 2\text{MCl}$ .

The best results were obtained with a cold saturated solution of sodium chloride, then comes potassium chloride, whilst calcium chloride gives the smallest yield. The carbon electrodes were very soon disintegrated.

The authors hope that they may succeed in utilising the chlorine which becomes valueless, in the form of calcium chloride, in Solvay's soda process, by converting it into its oxygen compounds. For this purpose they are at present engaged in more completely investigating the nature of the decomposition.

B. B.

### Existence of Nitrous Anhydride in the State of Vapour.

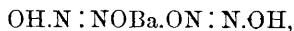
By G. LUNGE (*Ber.*, 15, 495—496).—Nitrous anhydride when passed into a solution of aniline and benzene behaves like a mixture of nitric oxide and nitric peroxide, diazobenzene nitrate being produced, and nitric oxide evolved.

It is not possible to distinguish by analysis between a mixture of NO and  $\text{N}_2\text{O}_4$ , and  $\text{N}_2\text{O}_3$ . But the author has shown experimentally that  $\text{N}_2\text{O}_3$  exists in the gases which escape from the sulphuric acid chambers; if it was a mixture of NO and  $\text{N}_2\text{O}_4$ , this could not possibly be the case, for this mixture would be completely converted into  $\text{N}_2\text{O}_4$  by the excess of oxygen present in the chamber. The author is therefore satisfied that  $\text{N}_2\text{O}_3$  can exist as a vapour.

D. A. L.

**Basicity of Hyponitrous Acid.** By W. ZORN (*Ber.*, 15, 1007—1011).—The author has described a compound obtained by the action of ethyl iodide on silver hyponitrite, whose vapour-density and chemical relation pointed to the formula  $\text{EtO.N:N.OEt}$ .

It would then appear that hyponitrous acid is a bibasic acid of composition  $\text{HO.N:N.OH}$ ; and in order to examine this view, the author has studied the action of potash on Frankland's dinitroethylic acid, which might be an acid alkyl salt of hyponitrous acid,  $\text{EtO.N:N.OH}$ . But experiment showed that dinitroethylic acid on saponification does not yield a hyponitrite, and is therefore not a derivative of the acid. The author, however, succeeded in obtaining in solution a hydrogen barium hyponitrite, by suspending the normal barium salt and adding sulphuric acid, and found that the reaction of the solution remained neutral so long as not more than 1 equivalent of sulphuric acid was added to 2 equivalents of the barium salt. As the hydrogen salt, like other hyponitrites, was readily decomposed, it could not be obtained in a fit state for analysis, although crystals of the salt were separated from the solution, but the ratio Ba:NO was found to be 4:1, and therefore the salt has the constitution



and hyponitrous acid is thus a bibasic acid.

V. H. V.

**Pernitric Acid.** By P. HAUTEFEUILLE and J. CHAPPUIS (*Compt. rend.*, **94**, 1306—1310).—On cooling a mixture of oxygen, nitrogen, and ozone charged with vapours of pernitric acid to  $-23^{\circ}$ , a small quantity of a highly volatile crystalline powder is condensed, but could not be isolated. In order to determine the composition of pernitric acid, it was absorbed in strong sulphuric acid immediately after electrification of a mixture of oxygen and nitrogen in known proportions, and the composition of the residual gas was determined.

The authors also measured the contraction when the ozone and pernitric acid had acquired their maximum tension, and then determined the volume of combined nitrogen. Both methods show that the pernitric acid has the composition  $\text{NO}_3$ . The authors have analysed a volatile crystalline substance containing the elements of pernitric acid and perchloric anhydride, and will shortly publish their results.

C. H. B.

**Behaviour of Sulphuric Monochloride with certain Elements.**

By K. HEUMANN and P. KOEHLIN (*Ber.*, **15**, 416—420).—Sulphuric monochloride is without action on sulphur in the cold, but on warming, a brisk reaction takes place, sulphurous anhydride and hydrochloric acid being given off, whilst sulphur dichloride,  $\text{S}_2\text{Cl}_2$ , passes over (b. p.  $138^{\circ}$ ). On warming sulphuric monochloride and phosphorus, violent reaction sets in attended with evolution of the same gas as with sulphur, but the experiment ends with the explosion of the apparatus. With amorphous phosphorus the action is quieter; the products are phosphorus oxychloride (b. p.  $110^{\circ}$ ), and phosphoric acid. With finely powdered arsenic the monochloride reacts, with evolution of sulphurous anhydride, whilst arsenic trichloride distils off and arsenious anhydride remains behind. The reaction appears to depend on the breaking up of the chlorosulphuric acid thus:  $2\text{SO}_2(\text{OH})\text{Cl} = 2\text{Cl} + \text{SO}_2 + \text{SO}_4\text{H}_2$ . Antimony behaves in a similar manner. Tin acts in the cold with production of tetrachloride in theoretical quantity, according to the equation:  $4\text{SO}_2(\text{OH})\text{Cl} + \text{Sn} = \text{SnCl}_4 + 2\text{SO}_2 + 2\text{SO}_4\text{H}_2$ .

This large yield is explained from the fact that tin tetrachloride is not so easily attacked by sulphuric acid as the chlorides of antimony and arsenic are. Tin tetrachloride is also produced when a stream of hydrochloric acid gas is passed into a solution of tin in fuming sulphuric acid. When sulphuric monochloride is heated with charcoal, it is decomposed, with evolution of sulphurous anhydride, hydrochloric acid, carbonic oxide, and carbonic anhydride. The monochloride therefore acts as a chlorinating agent with sulphur, arsenic, antimony, and tin.

D. A. L.

**Action of Potash on Lead Oxide.** By A. DITTE (*Compt. rend.*, **94**, 1310—1313).—When potash solution is added with continual agitation to lead hydrate,  $\text{PbH}_2\text{O}_2$ , suspended in water at  $25^{\circ}$ , the amount of lead oxide dissolved increases with the quantity of alkali added until the latter amounts to 300 grams per 1000 grams of water. At this point the amount of lead oxide dissolved decreases slightly, but afterwards increases as more alkali is added, and at the same time the amorphous hydrate is converted into transparent microscopic

crystals. When the quantity of potash added reaches 400 grams per 1000 grams of water, the amount of lead oxide dissolved again suddenly diminishes, but afterwards increases as more and more potash is added. The hydrate,  $\text{PbH}_2\text{O}_2$ , dissolves at first in the dilute potash solution, but as the concentration of the latter increases, it is converted into the hydrate  $3\text{PbO}, \text{H}_2\text{O}$ , and this in its turn is converted into the anhydrous oxide when the concentration of the potash passes a certain point. The same changes take place at all temperatures, but more readily the higher the temperature. The hydrate,  $3\text{PbO}, \text{H}_2\text{O}$ , separates out in the form of transparent, white flattened hexagonal prisms (sp. gr. at  $0^\circ = 7.592$ ), when a solution of potash containing 100–300 grams per 1000 grams of water is saturated with lead hydrate at a temperature insufficient for its decomposition, and allowed to cool.

The anhydrous oxide is obtained in several different forms depending on the temperature and the degree of concentration of the potash solution. When the hydrate is heated with a solution of about 130 grams of potash in 1000 grams of water, the oxide is obtained in small plates, with a greenish-yellow tinge; sp. gr. at  $0^\circ = 9.1699$ . With 230 grams potash in 1000 grams water, the oxide forms brilliant sulphur-yellow crystals; sp. gr. at  $0^\circ = 9.2089$ . With 300 grams potash in 1000 grams water, the oxide separates out on cooling in small, compact, heavy brownish-yellow needles; sp. gr. at  $0^\circ = 9.8835$ . If potash is added gradually to lead hydrate suspended in water at  $20^\circ$  until it amounts to 400 grams per 1000 grams of water, the anhydrous lead oxide separates out after several days in the form of a hard compact greyish-green crust, composed of large brilliant laminæ; sp. gr. at  $0^\circ = 9.5605$ . When a hot solution of 185 grams potash in 1000 grams water is saturated with lead oxide, the latter separates out on cooling in long dark green, almost black needles; sp. gr. at  $0^\circ = 9.4223$ .

All these different varieties of the oxide are formed of small thin transparent crystals, the colour varying with the thickness of the plates, which are rhombic, the ratio of the diagonals being about 1 : 3. All the crystals become red when heated, and sulphur-yellow on cooling; their sp. gr. increases the more they are heated.

When lead hydrate is boiled with a saturated solution of potash, it is converted into deep rose coloured plates, which are also formed under certain other circumstances. These crystals are either thin square tables or combinations of the cube with the octohedron; sp. gr. at  $0^\circ = 9.3757$ . They become yellow on cooling after being heated.

It is evident that anhydrous lead oxide,  $\text{PbO}$ , exists in two distinct crystalline forms, i.e., in distinct isomeric modifications similar to those which Berthelot has observed in the case of haloïd silver salts and some other compounds.

C. H. B.

**Action of Insoluble Metallic Sulphides on Acid Solutions of Nickel Sulphate in Presence of Hydrogen Sulphide.** By H. BAUBIGNY (*Compt. rend.*, 94, 1251–1253).—If the continued formation of nickel sulphide in a solution of the sulphate containing hydrogen sulphide is a function of the relation between the weights of the

acid and metal present, it follows that if at any time the sulphide already formed by the action of hydrogen sulphide on a neutral solution of the sulphate, is removed, precipitation will cease. On the other hand, if nickel sulphide is added to an acid solution of the sulphate in such quantity that the free acid and the metal added in the form of sulphide are in the proportions necessary to form neutral or very slightly acid sulphate, then precipitation of the sulphide by hydrogen sulphide will go on progressively. The author finds that both these reactions actually take place. In the second case the condition of the sulphide added is of importance; the compact crystalline form produces little or no effect. The nickel sulphide, however, acts chemically, and not simply by its presence. The author intends to show in a subsequent paper that a sulphydrate of nickel sulphide is formed: copper sulphide produces the same effect, but zinc sulphide exerts no similar influence.

It follows that hydrogen sulphide will not precipitate nickel with zinc in a neutral solution of their sulphates unless the zinc is present in quantity little inferior to that of the nickel. In all cases precipitation can be prevented by the addition of a small quantity of free acid. With mixtures of the sulphates of copper and nickel in any proportion, some of the nickel will be precipitated from a neutral solution, and precipitation can only be prevented by the addition of a considerable quantity of free acid. In this case also it is necessary to filter and wash as rapidly as possible in order to prevent the copper sulphide acting on the nickel.

C. H. B.

**Reactions of Mercuric Chloride.** By H. DEBRAY (*Compt. rend.*, 94, 1222—1224).—Mercuric chloride, as is well known, is reduced to mercurous chloride by sulphurous acid, especially on heating. If, however, sodium chloride is present in quantity about twenty-five times as great as the mercuric chloride, no reduction takes place even on boiling the liquid. This cannot be explained by the assumption that the double sodio-mercuric chloride is unattacked by sulphurous acid: for Berthelot has shown that the formation of the double chloride is accompanied by a development of heat less than 1 cal., whereas the reduction of mercuric chloride by sulphurous acid develops + 14.7 cal. If the mixture of sulphurous acid and chlorides is heated in a sealed tube at 120°, a crystalline precipitate of mercurous chloride is slowly formed. That no reduction takes place when the liquid is boiled under ordinary pressure is proved by the fact that the addition of potash, after expulsion of the sulphurous anhydride, produces a yellow precipitate of mercuric oxide, without any trace of mercurous oxide.

When potash or soda is added in excess to a solution of mercuric chloride mixed with a large quantity of sodium chloride, no oxy-chlorides are formed, and there is no immediate precipitate, but after a short time mercuric oxide is deposited in a crystalline form. The crystals are transparent and are denser than the ordinary precipitated oxide. If precipitated in the cold, they are yellow, but if precipitated from a boiling solution they have a red colour similar to that of the oxide prepared by igniting the nitrate. The red precipitated oxide is

not attacked by dry chlorine; the yellow crystalline variety is attacked, but very much more slowly than the amorphous yellow variety.

C. H. B.

**Tungsten-bronzes.** By J. PHILIPP (*Ber.*, **15**, 499—510).—These bronzes decompose ammoniacal silver solution with precipitation of silver and formation of sodium tungstate. The quantity of silver precipitated is always proportional to the amount of oxygen necessary for the complete oxidation of the compound. This fact is utilised for a method of analysis. The finely powdered bronze is boiled with a large excess of ammoniacal silver solution, and the precipitated silver is ignited and weighed; it, however, always contains tungstic acid, which is left as a residue on treating the silver with nitric acid and weighing; the quantity can be reduced to a minimum by treating the precipitated silver with ammonia, and filtering hot. The tungsten and sodium are estimated in the filtrate from the silver. After the greater part of the ammonia is driven off by evaporation, nitric acid is added to the solution, the whole boiled, the precipitated tungstic acid collected and weighed. The sodium is weighed as chloride.

The author frequently uses this process; but recommends Wöhler's process, in which the bronze is fused with sulphur, and the resulting mass decomposed with aqua regia, when there is sufficient material to make the sodium and tungstic determinations in separate portions.

By means of Wright's process, which consists in adding metallic tin to fused sodium tungstate, the author has prepared four kinds of tungsten bronze. When 30 grams tinfoil are added to 60 to 80 grams of a mixture (containing  $2\text{Na}_2\text{O}, 3\text{WO}_3$ ) heated to fusion, and the whole mass is kept at that point for an hour or two, *two yellow bronzes* are obtained. The one forms yellow cubes,  $\text{Na}_5\text{W}_6\text{O}_{18}$ , easily separated by heating with water, the other red-yellow crystals,  $\text{Na}_4\text{W}_5\text{O}_{15}$ , and can only be purified by successive boiling with hydrochloric acid and dilute soda. The fine powder of these bronzes is of a pale brown colour, and when stirred up in water makes the liquid of a beautiful blue colour by transmitted light. When 100 parts of a mixture of  $\text{Na}_2\text{WO}_4 + \text{WO}_3$ , are mixed under similar conditions with 30 parts tinfoil, and kept at fusion for three hours, both varieties are produced, the yellow in excess. When a mixture either of  $2\text{Na}_2\text{O} + 5\text{WO}_3$  or  $2\text{Na}_2\text{O} + 6\text{WO}_3$  is fused with tin, a red bronze,  $\text{Na}_2\text{W}_3\text{O}_9$  (the formula given by Malaguti to the yellow bronze), is obtained. In powder this is red and imparts to water, when suspended in that liquid, a green colour by transmitted light. The fusion of tin with the mixture  $\text{NaO} + 3\text{WO}_3$ , gives rise to a blue bronze,  $\text{Na}_2\text{W}_5\text{O}_{15}$ . Identical bronzes are obtained by the electrolysis of these mixtures, or by reduction with hydrogen. Fusion in a stream of hydrogen is especially favourable to the preparation of the yellow and red bronzes. Temperature plays an important part in this reaction: for if a very acid sodium tungstate is heated in a current of hydrogen and the temperature gradually increased, the salt first turns blue, then red, then yellow, and finally, at a higher temperature, black, owing to the separation of metallic tungsten. That



these bronzes differ from one another only by having more or less  $\text{WO}_3$  is evident from the fact that they are convertible. If the finely powdered blue or red bronze is fused with normal sodium tungstate, air being excluded, the yellow bronze is produced; if on the other hand, the yellow or red bronze be fused with excess of acid sodium tungstate, air being excluded, the blue bronze will be formed. For analysis of the blue bronze it is necessary to heat it at  $120^\circ$  in sealed tubes with the ammoniacal silver solution, in order to ensure complete decomposition.

D. A. L.

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## Mineralogical Chemistry.

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**Composition of Coal.** By O. HELM (*Arch. Pharm.* [3], 20, 37—39).—In a former communication on the amount of sulphur in asphalt (*Arch. Pharm.*, 213, 507) the author expressed the opinion that the sulphur existed therein in a state of organic combination, as well as in the forms of sulphide and sulphate. He has employed various methods requiring the use of solvents for the removal of such organically combined sulphur, but with no result; he was therefore obliged to determine it after estimating that quantity required to combine with the iron present and the amount present as sulphate. The samples analysed were Newcastle and Leverson's Wallsend; in the first was found 0.232 per cent.  $\text{FeS}_2$ , 0.105 of sulphuric acid, and 0.372 per cent. S organically combined; in the Wallsend organically combined sulphur was present to the amount of 0.118 per cent., and 0.102 per cent.  $\text{FeS}_2$ , with 0.033 per cent. sulphuric acid was found.

E. W. P.

**Analyses of Nephrites from Pile Dwellings.** By K. SEUBERT and G. LINK (*Ber.*, 15, 219—221).—These samples, consisting of stone axes, were found in pile dwellings at Maurach on the Lake of Constance. Only the analytical results are communicated in this paper:—

- I. Nephrite from pile dwelling. Colour, leek-green. Dried at  $120^\circ$ .
- II. Black-green variety of nephrite. Air dried.
- III. Leather-brown variety of nephrite. Had apparently been submitted to the action of fire. Dried at  $120^\circ$ .
- IV. Effloresced green nephrite. Air dried.
- V. Probably completely effloresced nephrite. The surface white and dusty, the interior was also much altered and in parts friable. Dried at  $120^\circ$ .

	I.	II.	III.	IV.	V.
SiO <sub>2</sub> .....	57·57	59·94	57·30	56·82	55·49
FeO .....	4·71	9·10	1·82	3·38	4·27
Fe <sub>2</sub> O <sub>3</sub> .....	0·95	—	3·32	5·45	0·96
CaO .....	12·62	12·26	12·45	12·48	13·89
MgO .....	22·25	21·20	23·44	20·41	21·71
Alkalis .....	0·46	0·50	0·16	0·11	0·62
CO <sub>2</sub> .....	—	—	—	trace	0·98
H <sub>2</sub> O .....	1·21	2·42	1·13	1·31	1·87
	99·77	100·82	99·62	100·46	99·79
Ratio SiO <sub>2</sub> : RO	1 : 0·972	1 : 1·112	1 : 0·988	1 : 0·984	1 : 0·972

In all cases the quantities of potassium and aluminium present were too small for estimation. An organic nitrogenous substance was present in all samples.

A. J. G.

**Ash ejected from Vesuvius, February 25th, 1882.** By L. RICCIARDI (*Compt. rend.*, **94**, 1321—1322).—This ash collected at the edge of the crater is black, magnetic, very rich in small crystals of leucite and fragments of augite and magnetite, and when moistened gives a distinct acid reaction. On heating, it gives off hydrochloric acid, and loses 1·35 per cent. It contains 3·13 per cent. matter soluble in water, consisting of free hydrochloric acid, ammonium sulphate and chloride, alumina, traces of iron, and a considerable proportion of lime, magnesia, potash, and soda. When treated in the cold with hydrochloric acid the ash effervesces slightly, and is partially decomposed with evolution of hydrogen sulphide. It evolves a sensible quantity of ammonia when treated with potash. The ash consists of—

SiO <sub>2</sub> .	SO <sub>3</sub> .	P <sub>2</sub> O <sub>5</sub> .	Cl.	Al <sub>2</sub> O <sub>3</sub> .	FeO.
47·84	0·17	1·83	1·32	18·67	5·07
Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	
4·38	9·42	3·77	5·64	2·04 = 100·15	

This ash, like all other substances ejected by Vesuvius from 1868 to 1882, contains a sensible quantity of phosphoric anhydride; on an average about 2 per cent., equal to 4·39 per cent. of normal calcium phosphate.

C. H. B.

**The Mineral Water of Schinznach.** By OBERLIN and SCHLAGDENHAUFFEN (*J. Pharm.* [5], **5**, 490—494).—The source of the arsenic in the deposit from this water (this vol., 589) is shown to be the water itself, which contains 0·00005 gram arsenic acid per litre, probably as calcium arsenate, = 0·0001 gram per litre.

The authors comment on the divergences between the analyses of this water by Loewig, Grandeau, and Bolley, with regard both to mineral and to gaseous constituents.

They show that the sulphuretted hydrogen is present in combination, since ferrous, cobalt, nickel, and manganese salts are immediately precipitated by the water, which also gives the violet coloration with sodium nitroprusside; also that the small amount of calcium sulphide found by Grandeau is insufficient to account for these reactions. As however all the gas must be in combination, they conclude that sodium sulphide is also present.

L. T. O'S.

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## Organic Chemistry.

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**New Carbo-silicon Compounds.** By A. COTSON (*Compt. rend.*, 94, 1316—1318).—When silicon is heated to bright redness on strongly compressed lamp-black, it is easy after cooling to separate a regulus which, when powdered and treated first with boiling potash, and then with hydrofluoric acid, leaves a slight residue containing carbon and silicon in varying proportions.

Hydrogen gas saturated with benzene vapour at  $50-60^{\circ}$  is passed over silicon contained in two dishes heated to bright redness in a porcelain tube. After about three hours the first dish contains a light black powder, the second a grey substance. Both these substances are sometimes found at opposite extremities of the same dish. They are purified by treatment with potash and hydrofluoric acid. The black powder consists of uncombined carbon mixed with the dark green compound  $\text{SiC}_2$ , which does not burn in a current of oxygen. Even when the hydrogen is quite dry the grey substance contains a considerable proportion of oxygen derived from the porcelain dish. Its composition varies, but it often contains more oxygen than corresponds with the formula  $\text{SiCO}_2$ . The most highly oxidised body obtained by Schützenberger and the author by the action of carbonic anhydride on silicon contains only 1 atom of oxygen for a molecule of carbo-silicon,  $\text{SiC}$ . It would therefore appear that the peroxidised compounds of the carbo-silicon series are formed in reducing atmospheres.

Powdered silicon is placed in a gas-carbon crucible lined with compressed lamp-black; this is placed inside several brasqued crucibles and heated to whiteness. The regulus of silicon is detached, freed from adhering charcoal, powdered, and purified by treatment with potash and hydrofluoric acid. The bottle-green powder thus obtained has the composition  $\text{Si}_2\text{C}_3\text{O}_2$ . Prolonged action of oxygen at a red heat gradually removes the excess of carbon.

If the silicon is replaced by a mixture of somewhat thick iron wire with lamp-black and silica, a crystalline compound is obtained, of the composition  $\text{Fe}_6\text{Si}_2\text{C}$  (sp. gr. = 6.6). This compound is formed only after prolonged heating at a very high temperature. C. H. B.

**Comparison of the Combining Energies of the Halogens and of Sodium with different Organic Residues.** By J. WISLICENUS (*Annalen*, 212, 239—250).—The numerous experiments made by the author and his pupils on the synthesis of acetoacetic ethers have shown that the combinations of the same halogen with various organic radicles, including those which are isomeric, exhibit, in regard to the energy and velocity with which they are produced, diversities as great as those which were observed by Menshutkin in the limiting values and initial velocities of etherification by the action of acids on alcohols and phenols (this Journal, 1880, Abstr., 375; 1881, 39, 144, 146, 883, and 1117), and by Hell and Urech in the rate of substitution of bromine in acids of the fatty series,  $C_nH_{2n}O_2$  (*ibid.*, 1880, 531). Further experiments on the action of alkyl haloids and the alkyl salts of  $\alpha$ -bromobutyric and  $\alpha$ -bromoisobutyric acids upon sodacetic ethers led to the following results:—

(1.) *Towards similar organic residues, the combining energy of chlorine is the greatest and that of iodine the least, as already known.* (2.) *Amongst compounds of the same halogen with isomeric radicles, the primary radicles show the least and the tertiary the greatest combining energies.* This is true, not only with regard to the alkyl iodides, but likewise for the bromobutyric acids. With respect to the isomeric  $\alpha$  bromobutyric acids, Hall and Urech likewise observed that the formation of bromoisobutyric acid takes place more quickly than that of normal bromobutyric acid.—(3.) *The combining energy of iodine and doubtless also that of the other halogens, for alcohol-radicles of the same category (primary or secondary) increases with the molecular weight, i.e., with increase of  $nCH_2$ .* The rate of this increase of combining energy however is not directly but inversely proportional to that of the molecular weight. Thus the difference in the times of reaction of the iodides of methyl and ethyl with ethylic acetosodacetate is proportionally much greater (4 or 4.5 to 39 minutes, or about 1 : 9) than that which is observed between the iodides of ethyl and normal propyl (30 to an average of 16.3, or about 1 : 4).—(4.) *The combining energy of the halogen is considerably less when the residue is an unsaturated primary alcohol radicle (allyl or benzyl for example), but is very considerably increased when the halogen is united to a primary but unsaturated carbon-atom (as in vinyl iodide).* (5.) *A diminution of combining energy is produced by linking of the  $CH_2$ -group united with the halogen to carboxyl, whether this linking be direct as in ethylic chloracetate, or made through the medium of  $CH_2$ , as in ethylic  $\beta$ -iodopropionate.*

In the preparation of dialkylised acetoacetic ethers, the author has frequently observed that the replacement of the second sodium-atom, introduced into the molecule subsequently to the first alkyl, takes place more readily than that of the first sodium-atom,—whence it appears that the sodium-atom in the molecule  $Me.CO.CXNa.CO.OEt$  is less firmly combined than that in sodacetoacetic acid ether,  $Me.CO.CHNa.CO.OEt$ ; and this conclusion is confirmed by the rise of temperature, amounting on the average to  $14.25^\circ$ , which takes place on mixing a solution of 4.6 g. sodium in 50 g. absolute alcohol with 31.6 g. ethylic ethylacetoacetate, whereas the formation of ethylic sodacetoacetate is attended with a rise of somewhat

more than 29 degrees. A still more rapid and energetic action is produced by treating the solutions of the sodethylacetoacetic ethers thus prepared with the same quantities of methyl and ethyl iodide as before.

Experiments on the action of alkyl iodides and bromobutyric ethers on sodio-malonic ethers led to precisely similar conclusions as to the dependence of the combining energy of a halogen on the nature of the organic residue to which it is attached. H. W.

**Production of Carbon Oxychloride from Chloroform.** By J. REGNAULD (*J. Pharm.* [5], 5, 504—506).—By passing the electric spark or silent discharge through a mixture of chloroform vapour and air, carbon oxychloride is formed, also when chloroform is treated with ozone. In absence of oxygen, chloroform is decomposed by the electric spark, with formation of hydrochloric acid and hexachlor-ethane.

The decomposition of chloroform, when exposed to the atmosphere in presence of sunlight, is due to the influence of ozone.

L. T. O'S.

**Constitution of the Nitro-products of the Fatty Series.** By I. KISSEL (*Journ. Russ. Chem. Soc.*, 1882, 226—230).—If nitro-ethane be prepared according to V. Meyer's method (*Annalen*, 171, 23), only a small yield is obtained (about 47 per cent. of the theoretical quantity), and, as the author finds, some of the volatile products of the reaction are easily lost. In order to avoid these disadvantages the author proposes to modify slightly V. Meyer's method. A capacious flask is filled with the requisite quantity of ethyl iodide and kept cool by a mixture of snow and ice. Then silver nitrite, previously dried in the dark at from 30—40°, is added gradually, and the flask is corked up and shaken briskly. After cooling, the addition of silver nitrite is repeated so slowly that no evolution of gas takes place. When the last portion of silver nitrite has been added, the shaking and cooling must be continued for some time. When the mixture does not get warm on further shaking, the flask is left in cold water for a day or so. After this time the product is distilled, first in a water-bath, then in an oil-bath. In order to remove completely the last quantity of ethyl iodide, the most volatile portion of the distillate is shaken with some fresh silver nitrite and redistilled. The distillate is submitted to fractional distillation, and the portions boiling at 108—113°, which are almost pure nitroethane, are collected separately. When the above process is carried on carefully, 54—66 per cent. of the theoretical amount of nitroethane is obtained. This circumstance, that the yield is larger than 50 per cent. seems to prove that the constitution of silver nitrite is not fairly represented by the formula:  $\text{Ag}_2\text{O} \cdot \text{NO} = \text{NO}_2 \cdot \text{Ag}$ , which has been proposed by V. Meyer (*Annalen*, 171, 27). One-half of the products boiling below 100° consisted of products boiling constantly at 29—30°. Although the appearance of the liquid and its odour seem to point to the presence of ethyl nitrite, its chemical reactions are more like those of nitroethane. The product boiling between 28—35° was washed with water, then with silver nitrate and a weak sodium carbonate solution, in order to remove the last traces of iodide, and after treating with dry silver nitrate, it was finally dried over

anhydrous calcium nitrate. After this treatment the liquid boils at 29—30°. Its analysis agrees with the formula  $C_2H_5NO_2$ . On treating it with sodium, a violent reaction takes place and the reactions of the white crystalline compound obtained are similar to those of sodium nitroethane. The same compound was obtained on treating the liquid with an alcoholic soda-solution.

Reactions similar to those described above take place on treating isopropyl nitrite, which was obtained as a secondary product in the preparation of secondary nitropropane and boiled at 43—44°, with metallic sodium or an alcoholic soda-solution.

The reactions of the sodium-derivatives of the compounds  $C_2H_5NO_2$ , one of which boils at 111—113°, and the other at 29—30°, are very much alike, and the same is the case as regards the sodium-derivatives of the compound  $C_3H_7NO_2$ , one of which boils at 115—118°, and the other 43—44°. This, according to the author's opinion, seems to point to the circumstance that the compounds in question are not ethereal salts of nitrous acid, but isomerides of nitroethane and nitropropane. If this explanation be found to be correct, by further investigation of the bodies, it will prove that the compounds discovered by V. Meyer are not nitro-compounds of saturated hydrocarbons.

There are many facts, indeed, which seem to show that "nitroethane" is acethydroxamic acid:  $CH_3.CO.NH(OH)$ . B. B.

#### Oxidation of Isodibutylene by Potassium Permanganate.

By A. BUTLEROFF (*Jour. Russ. Chem. Soc.*, 1882, 190—208).—The author's former researches on the oxidation of *isotributylene* have shown; that the nature of the products of oxidation varies according to the nature of the oxidising agent, chromic acid mixture yielding a peculiar solid acid,  $C_{11}H_{22}O_2$ , and a little acetone, whereas potassium permanganate does not yield either of these products. *Isodibutylene*, with chromic mixture, yields a crystalline acid, a neutral body and a little of the ketone  $C_7H_{14}O$ , and here again potassium permanganate gives different products.

Isodibutylene was treated with a solution of 5 parts of  $KMnO_4$  in 100 parts of water (9 parts of the salt for 5 parts of the hydrocarbon), first at the ordinary temperature and subsequently at 100°. Part of the hydrocarbon is completely oxidised. After complete decolorisation had taken place, the liquid was filtered from the oxides of manganese, and distilled (distillate A). The residue, consisting of potassium carbonate and a mixture of potassium salts of organic acids, was extracted by treatment with alcohol; the soluble salts were decomposed with dilute sulphuric acid; and the free acids extracted by ether and separated by fractional distillation. Amongst the acids separated were *acetic acid* and *trimethylacetic acid*, which is contained in the portion boiling from 140—180°. The portion boiling from 180—260° consists of *hydroxy-octylic acid* with some *trimethylacetic acid*.

From the first distillate A (see above), a new compound, which the author calls *oxoctenol*, was obtained. *Oxoctenol*,  $C_8H_{16}O_2$ , forms a crystalline mass, consisting of long thin prisms. It smells like camphor, and is easily soluble in alcohol and ether. It separates from the solution in strong acetic acid in beautiful long prisms. It is only



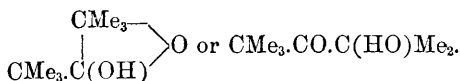
slightly soluble in water. It melts at  $49.5^\circ$ , and boils at  $178-178.5^\circ$  (corr.) without decomposition. Vapour-density = 4.8 at  $185^\circ$  (calculated 5.0).

*Oxoctenyl-acetate*,  $C_8H_{15}\overline{Ac}O_2$ , is obtained on heating the alcohol with acetic anhydride to  $150^\circ$ . It is a liquid having an aromatic odour, and boiling at  $200-202^\circ$ .

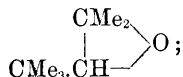
On heating oxoctenol with phosphorus pentachloride, an oily compound, probably  $C_8H_{15}Cl_3$ , is obtained; hydriodic acid yields the ether  $C_8H_{15}OI$ . As bromine does not act on oxoctenol, it must be regarded as a saturated compound.

*Oxoctylic acid*,  $C_8H_{16}O_3$ , separated from the distillate A by means of potash, forms fine white needles or glistening prismatic crystals, m. p. about  $107^\circ$ ; it is volatilised partly above  $300^\circ$ . It is easily soluble in alcohol, ether, and hot water. Its *potassium salt* forms scales, the *sodium salt* needle-shaped crystals. The last salt is hydrated and less soluble in water than the first. The *ammonium salt* forms a microcrystalline mass. The salts of *barium*, *calcium*, *magnesium*, and *zinc* are amorphous or crystallise with difficulty. The *lead salt* is difficultly soluble and crystalline. The *silver salt*,  $C_8H_{15}AgO_3$ , forms fine white needles.

As isodibutylene has the constitution  $CMe_3.CH : CMe_2$ , oxoctenol is either a product of oxidation or of hydration with oxidation, and has one of the following formulæ: either



The intermediate products are supposed to be: in the first case:



in the second case:  $CMe_3.CH_2.C(OH)Me_2$ .

According to experiments made for the author by Menschutkin, oxoctenol is a tertiary alcohol, because its limit of etherification with acetic acid is only 8.36 per cent.

For the constitution of oxoctylic acid the author assumes the formula  $CMe_3.CH_2.C(OH)Me.CO_2H$ .

Oxoctenol is interesting by its close relation to the camphors.

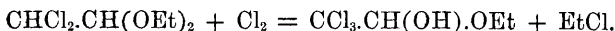
B. B.

**Ethyl Cyanate and Cyanurate.** By J. PONOMAREFF (*Ber.*, 15, 513—516).—By the action of cyanic bromide on sodium ethylate the author has obtained the same result as Mulder (this vol., 590). He proves that the product contains ethyl cyanate by converting it into urethane, thus:  $CNOEt + H_2O = NH_2COOEt$ . Ethyl cyanate forms a crystalline *mercurochloride*,  $C_3N_3(OEt)_3.HgCl_2$ , which tends to show that the molecule of the ethereal salt, in combination, is  $C_3N_3(OEt)_3$ . Ethyl cyanurate is regenerated from the mercurochloride by the action of ammonia gas. In the ethereal distillate from the product of the action of cyanogen bromide on sodium ethylate, the author has identified ammonia, solid cyanic chloride, and polymeric cyanic

bromide; both yield ethyl cyanurate by their action on sodium ethylate.

D. A. L.

**Bromochloral, Chlorobromal, Bromochloroform, and Chlorobromoform.** By O. JACOBSEN and R. NEUMEISTER (*Ber.*, **15**, 599—602).—It is well known that dichloroacetal is formed as an intermediate product in the preparation of chloral alcoholate, by the action of chlorine on alcohol, and that by the further action of chlorine, ethyl chloride and chloral alcoholate are obtained, thus:—



In a similar manner the action of bromine on dichloroacetal gives bromochloral alcoholate, and the action of bromine on monochloroacetal gives chlorobromal alcoholate.

*Bromochloral*,  $\text{CCl}_2\text{Br}.\text{COH}$ , obtained by decomposing the alcoholate with cold concentrated sulphuric acid, is a colourless liquid, having an odour similar to that of chloral, but inducing tears even more strongly. B. p. =  $126^\circ$ ; sp. gr. at  $15^\circ$  = 1.9176. It becomes yellow on exposure to light. In presence of sulphuric acid it polymerises to *metabromochloral*, which is an amorphous, porcelain-like, scentless mass, insoluble in water, alcohol, and ether; it is reconverted into bromochloral on heating to  $270^\circ$ . *Bromochloral hydrate*,  $\text{CCl}_2\text{Br}.\text{CH}(\text{OH})_2$ , is a hygroscopic crystalline mass, easily soluble in water, alcohol, and ether, but less soluble in chloroform, from which it crystallises in rhombic plates (m. p.  $51^\circ$ ). *Bromochloral alcoholate*,  $\text{CCl}_2\text{Br}.\text{CH}(\text{OH}).\text{OEt}$ , crystallises in fine silky needles (m. p.  $43^\circ$ ). *Bromochloralid*,  $\text{C}_5\text{H}_2\text{Cl}_4\text{Br}.\text{O}_3$ , obtained by heating a mixture of bromochloral and ordinary sulphuric acid containing a little of the fuming acid, crystallises in colourless prisms (m. p.  $122^\circ$ ).

*Chlorobromal*,  $\text{CClBr}_2\text{COH}$ , is a colourless liquid (b. p.  $148$ — $149^\circ$ ; sp. gr. 2.2793 at  $15^\circ$ ), similar to bromochloral, except that it does not undergo polymerisation in presence of sulphuric acid. *Chlorobromal hydrate*,  $\text{CClBr}_2.\text{CH}(\text{OH})_2$ , crystallises in small prisms (m. p.  $51$ — $52^\circ$ ). *Chlorobromal alcoholate*,  $\text{CClBr}_2.\text{CH}(\text{OH}).\text{OEt}$ , forms long needles (m. p.  $46^\circ$ ). Bromochloral and chlorobromal, like chloral, combine directly with amides. The compounds with acetamide crystallise from hot alcohol in leaflets, the melting point ( $158^\circ$ ) being identical with that of the corresponding compounds of bromal and chloral, which they also resemble in other respects. Bromochloral and chlorobromal hydrates give bromochloroform and chlorobromoform respectively when treated with potash. *Bromochloroform*,  $\text{CHBrCl}_2$ , is a colourless liquid (b. p.  $91$ — $92^\circ$ ; sp. gr. 1.9254 at  $15^\circ$ ) which gradually becomes yellow on exposure to light. *Chlorobromoform*,  $\text{CHBr}_2\text{Cl}$ , is a liquid similar to the preceding compound (b. p.  $123$ — $125^\circ$ , with slight decomposition; sp. gr. 2.445 at  $15^\circ$ ).

T. C.

**Action of Chlorine on Sulphonic Derivatives.** By W. SPRING and C. WINSSINGER (*Ber.*, **15**, 445—447).—The object of this work is to see if it is possible to determine experimentally the influence exerted on a molecule by certain atoms or groups of atoms in the molecule.

Pure ethylsulphonic acid is not acted on by chlorine of the sulphonic group, hence exerts its influence over the entire molecule. Iodine trichloride attacks it, and when in excess yields hexachlorethane. If, however, the iodine chloride is used in smaller quantity, dichlorethylsulphonic acid is always produced. This, when heated with barium hydrate, yields barium monochlorisethionate,  $C_2H_4Cl.SO_4Ba$ . When heated in sealed tubes with ammonia at  $100^\circ$  for one hour, it is converted into a crystalline monochlortaurine,  $C_2H_3Cl.NH_2.SO_3H$  (m. p.  $191-201^\circ$ ). By treatment with silver carbonate a mixture of silver chlorisethionate,  $C_2H_3(OH)Cl.SO_3Ag$ , and silver ethylsulphonate, is produced, showing that the body  $C_2H_3Cl_2SO_3Ag$  is easily attacked by water and transformed. This suggests that one chlorine-atom is next to the sulpho-group, and further that two chlorine-atoms and a sulpho-group cannot exist in the same molecule. Diethylsulphone is not attacked by chlorine; it is, however, decomposed by heating in a sealed tube with a sufficient quantity of iodine trichloride at  $140-150^\circ$ , for 7—8 hours, according to the equation  $(C_2H_5)_2SO_2 + 8ICl_3 = 2C_2Cl_6 + Cl_2SO_2 + 4I_2 + 10HCl$ . Treated in a similar way with less iodine chloride it yields trichlorethane,  $C_2H_3Cl_3$ , tetrachlorethane,  $C_2H_2Cl_4$ , monochlordiethylsulphone,  $Et.SO_2.C_2H_4Cl$ , sulphuric dichloride,  $SO_2Cl_2$ , and some unattacked diethylsulphone. In these cases the introduction of the sulphonic group seems to strengthen the union between the carbon and hydrogen, and hence to make the carbon more stable. Chlorine, on the other hand, seems to have a contrary influence. Chlorine decomposes an aqueous solution of ethyl sulphoxide with great facility; hydrochloric acid and ethyl chloride are evolved, and ethylsulphonic chloride separates out. With dry ethyl sulphoxide chlorine produces ethyl chloride and a chlorinated sulphinic acid.

D. A. L.

**Carbohydrate from Fucus Amylaceus.** By H. G. GREENISH (*Arch. Pharm.* [3], 20, 241—257).—The carbohydrate present in *Fucus amylaceus* has been described at different times, but as the results of the various researches have not been conclusive, the author undertook to reinvestigate the whole case. Microscopical examination shows the presence of starch granules. Treatment with cold water removes some albumin and ash, and a substance which, when boiled with ashes, reduces copper solution; this substance seems to be identical with the saccharifiable mucilage of all phanerogams. Neither mannitol, cane-sugar, nor grape-sugar is present in the cold extract. In a hot aqueous extract is to be found a carbohydrate identical with Payen's gelose, which is convertible into arabinose, and some other intermediate substance. Boiling water removes starch; the gelose is not identical with lichenin.

E. W. P.

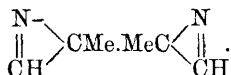
**Preparation and Properties of Ethylene-diamine.** By O. RHOUSSOPOULOS and F. MEYER (*Annalen*, 212, 251—256).—Hofmann, by heating 1 mol. ethylene dichloride with  $2\frac{1}{2}$ —3 mols. ammonia, obtained a mixture of the hydrochloride of mono-, di-, and tri-ethylene diamine and sal-ammoniac, in which the first of these hydrochlorides was present in small proportion only, 30 kg.  $C_2H_4Cl_2$  having yielded

not more than 1.5 kg.  $C_2H_4(H_2NCl)_2$ , or 1.5 per cent. of the ethylene dichloride employed. The authors of the present paper find that the yield of this compound may be increased by augmenting the proportion of ammonia present, this proportion being, however, limited by the necessity of operating in sealed tubes. Good results were obtained with 17—20 mols.  $NH_3$  to 1 mol.  $C_2H_4Cl$ .—By heating 42 g. of the dichloride in eight tubes, with 510 c.c. aqueous ammonia of 33 per cent., a product was formed, containing 53.6 g. of ethylene-diamine hydrochloride, or 127.6 per cent. of the ethylene dichloride used (calc. 134.3 per cent.).

The *hydroxide*,  $C_2H_4(H_2NOH)_2$ , obtained by heating the hydrochloride with sodium hydroxide, exhibited the properties described by Hofmann. It does not mix with benzene or ether, and cannot be extracted by ether from its aqueous solution. Boiling point  $118^\circ$  ( $117^\circ$  Hofmann). Sp. gr. 0.970 at  $15^\circ$ . Solidifies in a freezing mixture to a crystalline mass melting at  $+10^\circ$ . Anhydrous *ethylene-diamine*,  $C_2H_4(NH_2)_2$ , which Hofmann obtained by treating the hydroxide with sodium, may also be prepared by repeatedly heating the hydroxide with recently fused sodium hydroxide in a sealed tube for several hours at  $100^\circ$ . It has a density of 0.902; boils at  $116.5^\circ$ ; solidifies in a freezing mixture, and melts at  $8.5^\circ$ . Vapour-density = 2 (calc. 2.06). It does not mix with benzene or with ether.

H. W.

**Nitroso-compounds and Ketines.** By V. MEYER (*Ber.*, 15, 1047—1050).—The author has already shown that by the action of nitrous acid on the aceto-acetate three classes of substitution-products are formed: (1) nitroso-aceto-acetates; (2) nitroacetone and its homologues; (3) nitrosopropionic acid and its homologues. Of these substances nitrosopropionic acid behaves like other nitroso-compounds, in being converted by nascent hydrogen into amidopropionic acid; but nitroacetone yields neither an amidacetone nor its corresponding anhydride, but a base of formula  $C_6H_8N_2$ , belonging to the class of *ketines*. In this respect nitrosoacetone differs not only from other nitroso-compounds, but also from nitrophenylacetone. This difference may be explained by supposing the intermediate formation of a nitrosopinacone,  $OH.NH.CH_2.CMe(OH).CMe(OH).CH_2.NH.OH.Me$ , which loses  $4H_2O$ , and is converted into a ketine of composition



But this explanation seems to be precluded by the easy conversion of the nitroacetone into the ketine under conditions under which acetone is unaffected. If, however, the hypothesis is correct, then the introduction of the nitroso-group renders the CO group more easily reducible. On the other hand it may be supposed that the so-called nitrosoacetone does not contain a nitroso-, but an N.OH-group, an hypothesis which receives some support from the fact that nitrosoacetone differs in its behaviour towards sulphuric acid and phenol from other nitroso-compounds. In order to solve this difficulty,

and to throw light on the constitution of nitrosoacetone, the experiments described in the succeeding abstract were carried out.

V. H. V.

**Nitrosoacetone and Ketine.** By F. P. TREADWELL and E. STEIGER (*Ber.*, **15**, 1059—1061).—Nitrosoacetone heated with dilute hydrochloric acid yields acetic and formic acids and ammonia, thus:  $C_3H_5O(NO) + 2H_2O = C_2H_4O_2 + H_2CO_2 + NH_3$ . This decomposition is similar to that of nitrosomethylacetone (*Abstr.*, 1881, 895). From an ammoniacal solution of nitrosoacetone, silver nitrate throws down a silver salt,  $Me.CO.CHAg(NO)$ , as a golden-yellow precipitate, rapidly darkening in the air. Although the preparation of ketines from nitrosomethyl-, ethyl-, and propyl-ketones presents no difficulty, yet the authors were unable to isolate the ketine from nitrosoacetone,  $Me.CO.CH(NO)$ , owing to the readiness with which the free base decomposes; but only its platinumchloride,



in the form of golden-yellow leaflets, sparingly soluble in cold, readily soluble in hot water. Ketine, like its homologues dimethyl- and diethylketine, is a diacidic base; dipropylketine is however monacidic. The authors also draw attention to the gradations in chemical and physical properties of the homologous series of ketines.

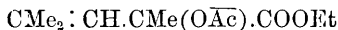
V. H. V.

**Presence of Furfural in Fermented Liquids.** By M. A. JORISSEN (*Ber.*, **15**, 574—576).—A reply to Förster's criticisms (*Ber.*, **15**, 574) on a paper by the author on this subject.

T. C.

**Condensation of Acetone.** By A. PINNER (*Ber.*, **15**, 576—586, and 586—595).—This is a continuation of previous work on this subject (*Abstr.*, 1881, 796). By the action of potassium cyanide on acetone saturated with hydrochloric acid gas, the following have been obtained:—1. *Mesitonic acid*,  $C_7H_{12}O_3$  (m. p.  $90^\circ$ ; b. p.  $230$ — $240^\circ$ ). 2. *Mesitylic acid*,  $C_8H_{13}NO_3.H_2O$ , already described by Simpson; sparingly soluble in water. Its *amide*,  $C_8H_{14}N_2O_2$ , forms warty crystals (m. p.  $222^\circ$ ), easily soluble in water and in alcohol. The ethylic salt,  $C_8H_{12}EtNO_3$ , melts at  $85^\circ$ , and boils at  $290^\circ$ . This amide and ethylic salt are likewise obtained directly by the action of potassium cyanide on the acetone saturated with hydrochloric acid, if the conditions of the experiment are slightly varied. 3. A cyanide,  $C_{11}H_{18}N_2O_2$ , which is very sparingly soluble in water and in alcohol, and from which phloronic acid,  $C_{11}H_{18}O_5$ , and other derivatives may be obtained.

*Mesitonic acid*,  $CMe_2:CH.CMe(OH).COH$ . That mesitonic acid has the constitution here assigned to it is proved by the fact that the *ethylic salt*,  $CMe_2:CH.CMe(OH).COOEt$  (colourless liquid, b. p.  $210^\circ$ ), may be readily converted into the *acetyl compound*,



(b. p.  $205$ — $207^\circ$ ). When mesitonic acid is distilled it loses water,

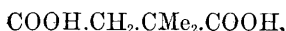
and forms the *anhydride*,  $CMe_2:CH.CMe \begin{smallmatrix} \diagup CO \\ | \\ \diagdown O \end{smallmatrix}$ , which crystallises in

colourless transparent prisms (m. p.  $24^{\circ}$ ; b. p.  $167^{\circ}$ ), emits a characteristic odour, is quite neutral, and is but sparingly soluble in water. On boiling with potash it is reconverted into the acid, and combines readily with bromine, forming an addition or a substitution-product, according to circumstances. Mesitonic acid itself likewise combines with bromine, but these compounds have not been further investigated.

*Mesitylic acid*,  $\text{Me}_2\text{C} < \begin{smallmatrix} \text{CH}_2 \\ \text{CO.NH} \end{smallmatrix} > \text{CMe.COOH}$ , on oxidation with an acid solution of potassium permanganate, gives chiefly *dimethylsuccinimide*,  $\text{Me}_2\text{C} < \begin{smallmatrix} \text{CH}_2.\text{CO} \\ \text{CO.NH} \end{smallmatrix} >$  (previously described), and on further oxidation *potassium dimethylmalonamate*,  $\text{CMe}_2(\text{COOH})\text{CONH}_2$ , which subsequently splits up into ammonia, carbonic anhydride, and isobutyric acid, a portion of which is further decomposed into acetic acid and carbonic anhydride.

Potassium dimethylmalonamate crystallises with  $2\text{H}_2\text{O}$  in brilliant prisms, which are very soluble in water, and moderately soluble in alcohol. At  $100^{\circ}$  it becomes anhydrous, and at higher temperatures is converted into potassium formate. On boiling with potash it gives dimethylmalonic acid,  $\text{CMe}_2(\text{COOH})_2$  (m. p.  $165^{\circ}$ , with decomposition; Markownikoff gives  $170^{\circ}$ ).

Dimethylsuccinimide, when boiled with potash, loses ammonia, and is converted into the unsymmetrical *dimethylsuccinic acid*,



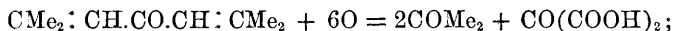
which is easily soluble in water, alcohol, ether, and benzene, and crystallises therefrom in colourless thick transparent prisms (m. p.  $140^{\circ}$ ); at  $190^{\circ}$  it loses water, and forms the *anhydride*.

Mesitylic acid gives mesitonic acid (m. p.  $88^{\circ}$ ) when heated with concentrated sulphuric acid at  $150^{\circ}$ . An attempt to prepare mesitylic acid directly from mesitylic oxide was unsuccessful.

Whilst mesitylic acid is attacked only by an acid, and not by a neutral or alkaline solution of potassium permanganate, phoronic acid, on the other hand, is oxidised only in presence of an alkaline solution, giving under these circumstances an acid having the composition  $\text{C}_9\text{H}_8\text{O}_4$ , which is easily soluble in water, melts with sublimation at  $190^{\circ}$ , and gives a well crystallised and sparingly soluble silver salt. The constitution of this acid has not yet been made out.

Residues obtained in the manufacture of phorone give on fractional distillation chiefly a portion boiling at  $245\text{--}255^{\circ}$  and having the composition  $\text{C}_{12}\text{H}_{18}\text{O}$ , and a portion boiling at  $310\text{--}320^{\circ}$  and having the composition  $\text{C}_{12}\text{H}_{20}\text{O}_2$ . The former of these substances, to which the name *xylitone* is given, is identical with the xylitol of Löwig (*Pogg. Ann.*, **44**, 404), and that of Weidmann and Schweizer (*ibid.*, **49**, 30; **50**, 275). The high-boiling body gives the same products on oxidation as xylitone, and probably bears the same relation to mesityl oxide that diacetone alcohol,  $\text{CMe}_2(\text{OH}).\text{CH}_2.\text{CMe}$ , bears to acetone. Oxidation of mesityl oxide with potassium permanganate in neutral solution gives acetic acid and oxyisobutyric acid (acetonic acid, m. p.  $76\text{--}77^{\circ}$ ); this confirms the formula  $\text{CMe}_2:\text{CH.CMe}$

usually assigned to mesityl oxide. Phorone when oxidised under similar circumstances gives chiefly carbonic anhydride, oxalic acid and acetone, the last in much the largest quantity: it is probable that acetone and mesoxalic acid are first formed, thus:



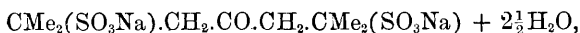
but the mesoxalic acid is at once further oxidised to oxalic acid and carbonic anhydride.

Not the least trace of acetic acid could be detected in the products of oxidation.

Contrary to the statement of Fittig (*Ann.*, **110**, 17), the author finds that mesityl oxide combines directly with hydrogen sodium sulphite to form *sodium isobutylmethylketone-sulphonate*,



This salt melts in its water of crystallisation at  $95^\circ$ , and then begins to decompose; it is very soluble in water and in alcohol; its aqueous solution is gradually decomposed on long boiling. Mesityl oxide is reproduced on boiling with a concentrated solution of potash. Phorone, like mesityl oxide, combines with hydrogen sodium sulphite to form *sodium diisobutylketonedisulphonate*,



which forms colourless prisms, and is very easily soluble in water, but less soluble in alcohol. Xylitin,  $\text{C}_{12}\text{H}_{18}\text{O}$ , apparently combines with hydrogen sodium sulphite to form a trisulphonate, but no definite results could be obtained.

T. C.

**Liquor Aluminii Acetici.** By T. POLECK (*Arch. Pharm.* [3], **20**, 257—268; and by VULPIUS, *ibid.*, 268—270).—The first paper is an inquiry into the different methods employed in Germany for the preparation of the above drug, as it appears that there are several ways by which it is prepared: precipitation of lead acetate with alum; precipitation of calcium acetate by aluminium sulphate; and separation of colloidal alumina from sodium aluminium carbonate by dialysis and addition of acetic acid. By neither of these processes is a pure product obtained, and the solutions are all dilute; moreover, they cannot be kept long without decomposition.

In the second paper Vulpius gives the formula which he used for the production of this liquor, and by it prepares what he considers to be a very pure and cheap preparation.

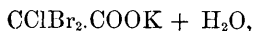
E. W. P.

### Bromodichloroacetic Acid and Chlorodibromoacetic Acid.

By R. NEUMEISTER (*Ber.*, **15**, 602—604).—*Bromodichloroacetic acid*,  $\text{CCl}_2\text{Br}\cdot\text{COOH}$ , obtained by oxidising bromochloral with fuming nitric acid, crystallises from nitric acid in large four-sided prisms, melts at  $64^\circ$ , and boils at  $215^\circ$  with slight decomposition. It is very hygroscopic, and blisters the skin. It is very soluble in water and in alcohol, but much less so in concentrated nitric acid. On boiling with water, and more especially with alkalis, it splits up into

bromochloroform and carbonic anhydride. Zinc dissolves in the aqueous solution of the acid without evolution of hydrogen, forming zinc bromide and dichloroacetic acid. The salts mostly crystallise well, and their solutions decompose on heating. The *potassium salt*,  $\text{CCl}_2\text{Br}.\text{COOK} + 3\text{H}_2\text{O}$ , crystallises in long rhombic prisms, which are easily soluble in water, less soluble in alcohol. The *sodium salt*,  $\text{CCl}_2\text{Br}.\text{COONa} + 5\text{H}_2\text{O}$ , forms large leaflets, which are easily soluble in water and alcohol, and moderately soluble in ether. It melts at  $100^\circ$ , and becomes anhydrous at  $120^\circ$ . The ammonium, zinc, lead ( $\text{CCl}_2\text{Br}.\text{COO}_2$ ) $\text{Pb} + \text{H}_2\text{O}$ , calcium and barium salts were also prepared. The *ethylic salt*,  $\text{CCl}_2\text{Br}.\text{COOEt}$ , is a colourless liquid (b. p.  $188\text{--}189^\circ$ ), emitting a weak peppery odour. *Bromodichloroacetamide*,  $\text{CCl}_2\text{Br}.\text{CONH}_2$ , obtained by the action of ammonia on the ethylic salt, crystallises in leaflets (m. p.  $139^\circ$ , b. p.  $253\text{--}255^\circ$  with partial decomposition), which are very soluble in ether, moderately soluble in alcohol, and insoluble in chloroform.

*Chlorodibromoacetic acid*,  $\text{CClBr}_2.\text{COOH}$ , is similar to bromodichloroacetic acid, and crystallises from concentrated nitric acid in rhombic plates (m. p.  $89^\circ$ , b. p.  $232\text{--}234^\circ$  with partial decomposition); it gives chlorobromoform on treatment with potash. Its aqueous solution dissolves zinc without evolution of hydrogen, forming first chlorobromoacetic acid, and then monochloroacetic acid. The *potassium salt*,



crystallises in brilliant prisms, which are permanent in the air, but fall to powder over sulphuric acid. It is moderately soluble in water and in alcohol, and loses its water of crystallisation at  $90^\circ$ . The *sodium, calcium, zinc, and lead salts* ( $\text{CClBr}_2.\text{COO}$ ) $_2\text{Pb} + \text{H}_2\text{O}$ , were also prepared and described. The *ethylic salt*,  $\text{CClBr}_2.\text{COOEt}$ , is a colourless liquid (b. p.  $203^\circ$ ).

*Chlorodibromacetamide*,  $\text{CClBr}_2.\text{CONH}_2$ , is insoluble in water, very easily soluble in ether, and less soluble in alcohol, from the last of which it crystallises in small quadratic leaflets (m. p.  $125^\circ$ ).

T. C.

**Nitrosobutyric Acid.** By S. WILÖGEL (*Ber.*, 15, 1057—1058).—In order to prepare nitrosobutyric acid, ethylic ethylacetoacetate is mixed gradually with a dilute solution of alcoholic potash; a solution of sodium nitrite is then added, and the mixture acidified with nitric acid and allowed to stand for a day or two. Silver nitrosobutyrate is then precipitated from the solution by the addition of silver nitrate; the free acid is obtained by decomposing this salt with hydrochloric acid. The acid forms silky twin needles (m. p.  $151^\circ$ ), easily soluble in alcohol, sparingly soluble in ether and water. The silver salt forms a white powder, scarcely altered by light, insoluble in water, soluble in nitric acid.

V. H. V.

**Action of Water on Isobromocaproic Acid.** By E. HJELT (*Ber.*, 15, 619—621).—When liquid dibromocaproic acid is heated with water, or better with water containing a little sodium carbonate, it gives a mixture of two lactones, one boiling at  $220^\circ$ , and the other with decomposition at a somewhat higher temperature. The small



quantity of material at disposal rendered a separation of the two lactones impossible. The residue left in the retort appeared to consist of a mixture of an oxylactone,  $C_6H_{12}O_4$ , and an unsaturated lactone,  $C_6H_{10}O_3$ . The mixture of lactones gave succinic acid when oxidised with nitric acid. Dibromocaproic acid when treated as above described, gives several acids as well as a mixture of lactone. The calcium salt,  $(C_6H_7O_2)_2Ca + H_2O$ , of one of these acids which is volatile in steam, is isomeric, although not identical, with calcium sorbate. The acids which are not volatile in steam, are at least two in number, one of which forms a crystalline (Engelhorn's oxyhydrosorbic acid, *Annalen*, **200**, 55), and the other an amorphous potassium salt, the latter of which contains less potassium, and is probably a salt of a dihydroxycaproic acid.

Solid dibromocaproic acid, obtained from sorbic acid, likewise gives a lactone when treated with water; on oxidation this gives a mixture of succinic and oxalic acids. The general conclusion is drawn that all bromocaproic acids obtained from sorbic or from hydrosorbic acids give lactones when heated with water or with alkalis. T. C.

**Decomposition of Monohalogen-substituted Crotonic Acids by Alkalis.** By R. FRIEDRICH (*Ber.*, **15**, 218—219).— $\beta$ -Chlorocrotonic acid (m. p.  $94.5^\circ$ ) and  $\beta$ -chloroisocrotonic acid (m. p.  $59.5^\circ$ ) yield the same decomposition products, but the reaction commences with the first at  $70-80^\circ$ , and with the iso-acid not until  $120-130^\circ$ . With dilute aqueous potash (6—7 per cent.) they both yield tetrolic acid (m. p.  $76.5^\circ$ ); concentrated potash (40—50 per cent.) gives mainly acetone and a little tetrolic acid. With concentrated alcoholic potash  $\beta$ -chlorisocrotonic acid yields a new ethoxy-acid,  $C_6H_{10}O_3$ , melting with decomposition at  $137.5^\circ$ , and on long contact with water and a trace of a mineral acid, it completely decomposes into carbonic anhydride, acetone, and alcohol. The homologous methoxy-acid prepared in a similar manner melts at  $128.5^\circ$ .

$\alpha$ -Methyl- $\beta$ -chlorocrotonic acid (m. p.  $69.5^\circ$ ) when treated with concentrated aqueous potash at  $140^\circ$  yields methylethylketone and carbonic acid, not monochlorobutylene as stated by Demarçay (this *Journal*, 1877, **2**, 591).

$\alpha$ -Chlorocrotonic acid (m. p.  $97.5^\circ$ ) from butylchloral decomposes with aqueous potash at  $190-222^\circ$ , yielding carbonic acid, much acetic acid, oxalic acid, and a syrupy acid which could not be purified.

Tetrolic acid is completely decomposed by aqueous potash at  $105^\circ$  into acetone and carbonic anhydride; oxidation with potassium permanganate converts it into carbonic anhydride, oxalic acid, and acetic acid. A. J. G.

**Action of Bromine on Carbon Bisulphide.** By C. HELL and F. URECH (*Ber.*, **15**, 987—994).—In a former communication the authors have shown that by the action of bromine on carbon bisulphide, a crystalline compound of formula  $C_2S_3Br_6$  is obtained; they have further examined the influence of the relative proportions of the reagents, the time, and the temperature. It is determined that the

action is not instantaneous, but requires several days, that a temperature of  $100^{\circ}$  not only impedes the velocity of the reaction, but also diminishes the quantity of the product, and that a mixture in the proportion  $\text{CS}_2 : 2\text{Br}_2$  reaches its reaction limit in the shortest time. Various tables showing the products under different conditions are given in the memoir.

V. H. V.

**Action of Hydrobromic Acid and Bromine on Diallylacetic Acid.** By E. HJELT (*Ber.*, 15, 627—629).—*Bromodipropylacetolactone*,  $\text{C}_8\text{H}_{13}\text{BrO}_2$ , is obtained by the action of hydrobromic acid on diallylacetic acid. It is a thick oil which does not solidify at  $-13^{\circ}$ ; is insoluble in cold, but sparingly soluble in hot water. It is slowly attacked by hot but not by cold caustic soda; and when boiled with an aqueous solution of an alkaline carbonate, gives an acid free from bromine, and an unsaturated lactone,  $\text{C}_8\text{H}_{12}\text{O}_2$  (b. p.  $235-240^{\circ}$ ). *Tribromodipropylacetolactone*,  $\text{C}_8\text{H}_{11}\text{Br}_3\text{O}_2$ , obtained by the action of bromine on diallylacetic acid dissolved in carbon bisulphide or chloroform, is a neutral oil which does not solidify at  $-13^{\circ}$ , and is insoluble in water. *Trioxydipropylacetolactone*,  $\text{C}_8\text{H}_{11}(\text{OH})_3\text{O}_2$ , obtained from the tribromocompound is identical with the lactone resulting from the decomposition of barium tetroxydipropylmalonate.

T. C.

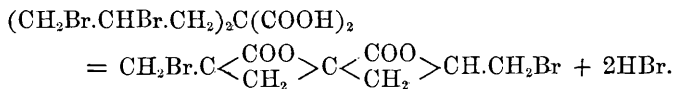
**Caprolactone.** By E. HJELT (*Ber.*, 617—618).—This lactone,  $\text{C}_6\text{H}_{10}\text{O}_2$ , which was obtained from the monobromide of hydrosorbic acid, has a vapour-density of 4.1 (calculated 3.94). It is soluble in 5—6 volumes of water, the solution gradually assuming an acid reaction owing to conversion into the hydroxy-acid. The lactone combines with sodium, with evolution of hydrogen, but is not decomposed when heated with alcoholic ammonia at  $150^{\circ}$ , nor when heated with hydriodic acid and amorphous phosphorus at  $200^{\circ}$ , proving that it possesses considerable stability. On boiling it with caustic alkalis it is readily converted into the salts of the corresponding hydroxycaproic acid. The neutral lactone is reproduced when barium hydroxycaproate is warmed with sulphuric acid.

In the formation of the lactone from monobromocaproic acid, it is accompanied by a considerable quantity of an unsaturated acid, which gives a calcium salt,  $(\text{C}_6\text{H}_9\text{O}_2)_2\text{Ca} + \text{H}_2\text{O}$ , having the same composition as calcium hydrosorbate, but differs from the latter in being more soluble in hot than in cold water. The free acid (m. p.  $-10^{\circ}$ , b. p.  $208-210^{\circ}$ ; hydrosorbic acid remains solid at  $-13^{\circ}$ , though Fittig and Borrringer, *Annalen*, 161, 309, state that it does not solidify at  $-18^{\circ}$ ); it combines with hydrobromic acid to form the same bromocaproic acid as hydrosorbic acid does. This bromocaproic acid gives caprolactone when treated with water. From these facts it would appear that the two acids are not identical, and that the isomerism depends on a difference in the position of the double linking.

T. C.

**Dilactones.** By E. HJELT (*Ber.*, 15, 625—627).—The dibromide of a dilactone,  $\text{C}_8\text{H}_{10}\text{Br}_2\text{O}_4$ , is obtained by the action of bromine on diallylmalonic acid dissolved in water, acetic acid, or carbon bisulphide. It is neutral, and crystallises in silky leaflets (m. p.  $130^{\circ}$ ), which are

insoluble in water, and very sparingly soluble in ether, but easily soluble in warm alcohol. The same bromide is obtained by the action of bromine on diethylic diallylmalonate. It is the first example of a dilactone, its formation being represented thus:—



It is probable that the tetrabromide is first formed, although it could not be isolated.

The dilactone (m. p. 105–106°, and b. p. above 360°), corresponding with the above dibromide, is obtained on the addition of water to a saturated solution of diallylmalonic acid in fuming hydrobromic acid. It is sparingly soluble in cold water, cold alcohol, or ether, but easily soluble in boiling water or hot alcohol. It is neutral, and when boiled with barium hydrate gives barium carbonate and oxy-lactones.

T. C.

**Boiling Points of the Lactones.** By E. HJELT (*Ber.*, 15, 629).—The simple lactones at present known all boil higher than the unsaturated acids isomeric with them. The statement made by L. Meyer (*Mod. Theor. Chem.*, 4th Ed., 278) that a hydroxyl compound always boils higher than an isomeric compound not containing hydroxyl does not hold good therefore in the case of the lactones.

T. C.

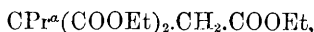
**Chloromalonic Acid and its Derivatives.** By M. CONRAD and M. GUTHZEIT (*Ber.*, 15, 605–607).—*Monochloromalonic acid*,  $\text{CHCl}(\text{COOH})_2$ , obtained by adding the corresponding ethylic salt to an alcoholic potash solution, and subsequent treatment of the potassium salt with hydrochloric acid, is easily soluble in water, alcohol, and ether. It melts at 133°, and forms monochloroacetic acid (m. p. 61°, b. p. 187°), when heated at 180° until carbonic anhydride is no longer evolved. *Imidodimalonamide*,  $(\text{NH}_2\text{CO})_2\text{CH}.\text{NH}.\text{CH}(\text{CONH})_2$ , is obtained by heating ethyl chloromalonate with alcoholic ammonia in sealed tubes at 135°. It crystallises from hot water in prisms, which carbonise at a high temperature without fusion. *Amidomalonamide*,  $\text{CH}(\text{NH}_2)(\text{CONH}_2)_2$ , obtained like the preceding compound, although under slightly different conditions, forms shining prismatic crystals (m. p. 182°), which are easily soluble in hot water.

T. C.

**Action of Bromine on Allylmalonic Acid.** By E. HJELT (*Ber.*, 15, 624–625).—*Dibromallylmalonic acid*,  $\text{C}_3\text{H}_5\text{Br}_2.\text{CH}(\text{COOH})_2$ , is obtained, together with an oil containing less bromine, by the action of bromine on allylmalonic acid dissolved in carbon disulphide. It crystallises in needles (m. p. 119–121°), which are moderately soluble in water, and very easily in ether; when boiled with water, it is converted into the above-mentioned oil, which was probably the compound  $\text{O} < \begin{smallmatrix} \text{C}_3\text{H}_5\text{Br} \\ \text{CO} \end{smallmatrix} > \text{CH}.\text{COOH}$ ; on boiling it with baryta-water, however, it gives the barium salt of dihydroxypropylmalonic acid, which when

boiled in aqueous solution loses a molecule of water, and forms a monobasic lactonic acid. T. C.

**Propyl- and Isopropyl-succinic Acid.** By G. WALTZ (*Ber.*, 15, 608—609).—*Triethylic propylethenyltricarboxylate*,



is obtained by the action of sodium ethylate and propyl iodide on triethylic ethenyltricarboxylate. It is a colourless oil boiling with partial decomposition at  $280^\circ$ . On saponification it gives *propylethenyltricarboxylic acid*,  $\text{CPr}^a(\text{COOH})_2\text{CH}_2\text{COOH}$ , which crystallises in slender interlacing needles melting at  $148^\circ$ , easily soluble in water and in ether. By continued heating, the free acid loses carbonic anhydride, and is converted into *propylsuccinic acid*,  $\text{COOH.CHPr}^a\text{CH}_2\text{COOH}$ , which forms warty crystals (m. p.  $91^\circ$ ); the neutral solution of the ammonium salt gives no precipitate with barium or calcium chloride, but is precipitated by neutral copper, lead and silver salts. Triethylic isopropylethenyltricarboxylate, which could not be obtained pure, was converted directly by the above reaction into a mixture of succinic and *isopropylsuccinic acids*,  $\text{COOH.CHPr}^b\text{CH}_2\text{COOH}$ , which were easily separated by the difference in solubility of their barium salts. The latter acid (m. p.  $114^\circ$ ) is crystalline and easily soluble in water, alcohol, and ether. Although melting at the same temperature it does not appear to be identical with pimelic acid, as is proved by the difference in solubility of the respective salts. T. C.

**Oxypropylmalonic Acid and its Lactone.** By E. HJELT (*Ber.* 15, 621—623).—The lactonic acid,  $\text{O} < \begin{smallmatrix} \text{C}_3\text{H}_6 \\ \text{CO} \end{smallmatrix} > \text{CH.COOH}$ , corresponding to oxypropylmalonic acid, is obtained when allylmalonic acid is dissolved in fuming hydrobromic acid, and subsequently boiled with water. It is a thick syrup, which could not be solidified, and is easily soluble in water, but only sparingly soluble in ether. The *barium salt*,  $\text{C}_6\text{H}_5\text{O}_5\text{Ba}^*$ , obtained by boiling the acid with baryta-water, crystallises in a network of fine needles, which are anhydrous and only sparingly soluble either in hot or cold water, and are insoluble in alcohol. The *barium salt*,  $(\text{C}_6\text{H}_7\text{O}_4)_2\text{Ba}$ , obtained by neutralising the acid with barium carbonate in the cold, crystallises in leaflets, which are more easily soluble in water and alcohol than the preceding compound. The *calcium*,  $(\text{C}_6\text{H}_5\text{O}_5\text{Ca})$ , and *silver*,  $\text{C}_6\text{H}_5\text{O}_5\text{Ag}_2$ , salts were also prepared, the former being more readily soluble in cold than in warm water. The free acid when heated to  $200^\circ$ , is decomposed into carbonic acid and valerolactone, which boils at  $207^\circ$  (corr.), and does not solidify at  $-18^\circ$  (b. p. =  $206-207^\circ$ ; Messerschmidt and Wolff, *Annalen*, 208, 92, and 104), and is easily soluble in water. The formation of valerolactone from the above lactonic acids shows that the lactone-oxygen is in the  $\gamma$ -position. T. C.

**Dry Distillation of Tartaric Acid.** By L. LIEBERMANN (*Ber.*, 15, 428—434).—The tartaric acid is mixed with powdered glass and

\* This is apparently the basic salt  $\text{C}_6\text{H}_7\text{O}_4\text{Ba.OH}$ .

distilled, water, carbonic oxide, and anhydride are given off. The distillate is filtered to separate the tarry matter. The filtrate after slight evaporation deposits crystals of *pyrotartaric acid*, which are filtered off. The second filtrate is neutralised with lead carbonate, and extracted with ether. *Lead pyruvate* is soon deposited from the aqueous solution. The filtrate from this salt is decomposed with sulphuric acid, filtered, and distilled. The distillate contains *formic* and a small quantity of *acetic acid*. The residue in the retort contains *lactic acid*, recognised by the form of crystallisation of the zinc salt. The ethereal extract deposited crystals of lactic anhydride, and left on evaporation a resinous residue, which had reducing properties, probably due to an aldehyde. 250 grams of tartaric acid yielded 9.24 grams pyruvic acid; 2.11 grams pyrotartaric acid; 4 grams formic acid; 4.0 grams tarry matter; 2.0 grams resin, aldehyde, and volatile acids.

D. A. L.

**Ethyl Nitrosoacetoacetate.** By S. WLEÜGEL (*Ber.*, 15, 1050—1056).—In order to prepare ethyl nitrosoacetoacetate the author adopts the following process:—

50 grams ethyl acetoacetate are dissolved gradually on a solution of soda (16 grams NaOH in 800 c.c. H<sub>2</sub>O), and to this is added a solution containing 29 grams NaNO<sub>2</sub> in 200 c.c. H<sub>2</sub>O. To the cooled mixture 200 c.c. of 20 per cent. sulphuric acid are then added, the unaltered acetoacetate removed with ether, and the mixture again acidified, and the ethyl nitrosoacetoacetate is then extracted with ether and crystallised sulphuric acid.

Ethyl nitrosoacetoacetate, on reduction with tin and hydrochloric acid, yields a compound of the formula C<sub>12</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>, which crystallises in long colourless needles melting at 85.5°, boiling at 315—317°, soluble in alcohol and ether. This substance behaves as an ethyl salt of an acid, and yields on saponification ethyl alcohol and a *ketone-dicarboxylic acid*.

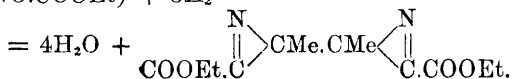
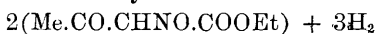
This latter compound, C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub>, crystallises in glistening cubes with 2 mols. of water; the anhydrous acid melts at 200°.

The barium, potassium, and ammonium salts crystallise in needles; silver nitrate forms a white, cobalt nitrate a red crystalline, ferric chloride an amorphous golden, and copper sulphate a green precipitate. On heating the free acid, it decomposes with evolution of carbonic anhydride, probably thus: C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub> = 2CO<sub>2</sub> + C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>.

With regard to the constitution of the acid, the view that ethyl nitrosoacetoacetate is reduced to the corresponding amido-compound,

which yields an anhydride,  $\text{MeC} \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{COOH} \end{array}$ , is excluded by the results

of analysis, which point to the formation of an acid, C<sub>4</sub>H<sub>4</sub>NO<sub>2</sub> (or more probably C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub>), and not C<sub>4</sub>H<sub>5</sub>NO<sub>2</sub>. It is probable that the reduction of ethyl nitrosoacetoacetate may be expressed thus:—



The ketine will then have the constitution of a dimethylpyridine, in which one of the CH groups is replaced by nitrogen; a view which is supported by the similarity in chemical properties and physiological action of the ketines with those of the pyridine derivatives.

V. H. V.

**Preparation of Amides of Monobasic Acids of the Paraffin Series.** By A. W. HOFMANN (*Ber.*, 15, 977—984).—Of the three methods of preparation of the amides, viz. (1), distillation of ammonium salt; (2) treatment of ethereal salt with ammonia; (3) action of ammonia on the acid chloride,—the first two are the most practical, whilst the third not only involves great loss of material, but the product is liable to be contaminated with ammonium chloride and secondary amides.

In the second process a considerable portion of the ethereal salt is converted into the corresponding alcohol and ammonium salt of the acid, and the yield is never more than 70 per cent. of that required by theory; and if the ethereal salt be sparingly soluble in water it is but slightly attacked even by concentrated ammonia solution. In the first process a stream of ammonia is given off at the commencement of the distillation, and only about 25 per cent. of the theoretical yield is obtained.

The author has found that the amides are most conveniently obtained by heating the dry ammonium salt under pressure at a temperature of 250°; the tube at the end of the reaction contains an aqueous solution of the amide and the ammonium salt, which may be separated by the sparing solubility of the former in water. The yield by this process is often as much as 80—85 per cent. An account of the preparation and a synopsis of the literature of various amides of the monobasic acids of the fatty series are given in the paper. Among new substances described is *disobutyramide*, obtained together with isobutyramide, by the action of ammonia on isobutyric chloride; it may be separated from the former by its insolubility in water; it crystallises from alcohol in long glistening needles (m. p. 174°), sublimes very readily, and on distillation decomposes into isobutyric acid and isobutyronitrile.

By the digestion of ammonium caprylate a crystalline amide (m. p. 94°) is obtained, differing from that (m. p. 110°) which Filletar prepared by the action of ammonia on ethyl caprylate. A monoxylamide, the corresponding acid of which was obtained from castor oil, is described as a pearly crystalline mass (m. p. 99°), insoluble in cold, soluble in hot water.

V. H. V.

**Action of Bromine in Alkaline Solution on Amides.** Part II. By A. W. HOFMANN (*Ber.*, 15, 407—416).—The author has observed that the acetyl-methylcarbamide resulting from the action of an alkaline solution of bromide on acetamide, is the final product of a series of reactions. It was hence desirable that an inquiry should be made into the different phases of the process in order to get some idea of the working of the reaction. The results of such an investigation are published in this paper.

Acetamide dissolves in bromine without development of heat or

evolution of hydrobromic acid; it is therefore probable than an addition product is formed; the compound, however, is of very loose combination, for on exposure to the air bromine evaporates and acetamide remains.

A mixture of 1 mol. bromine with 2 mol. acetamide, when treated with potassium hydroxide in the manner described in the previous paper (*loc. cit.*), gives rise to acetylmethyl-carbamide, as already observed. When, however, potassium hydroxide acts on a mixture of 1 mol. bromine with 1 mol. acetamide, *acetomonobromamide*,  $\overline{\text{Ac}}\text{NHBr}$ , is produced, which forms large well-formed rectangular plates, with characteristic striæ. It can, with care, be crystallised from warm water. The crystals contain 1 mol.  $\text{H}_2\text{O}$  (m. p.  $70-80^\circ$ , with loss of water), which is completely driven off at  $50^\circ$ , the dry substance melts at  $108^\circ$ . It is volatile, slightly even at  $50^\circ$ . The formation of this substance explains the production of methyl-acetocarbamide, which is immediately produced when molecular proportions of the monobromo-compound and acetamide are warmed with soda. *Acetomonochloramide*,  $\overline{\text{Ac}}\text{NHCl}$ , is formed where acetomonobromamide is treated with hydrochloric acid as long as a separation of bromine takes place; also by treating fused acetamide with chlorine: in this latter case the presence of alkali is not necessary, for the acetamide itself acts as such, and combines with the hydrochloric acid. Acetomonochloramide is crystalline, and melts at  $110^\circ$ . By further action of hydrochloric acid it is converted into acetamide, with evolution of chlorine. Iodine gives no definite results with acetamide. Ammonia acts violently on acetobromamide, nitrogen being evolved, and acetamide and hydrobromic acid formed:  $3\overline{\text{Ac}}\text{NHBr} + 2\text{NH}_3 = 3\text{HBr} + 3\overline{\text{Ac}}\text{NH}_2 + \text{N}_2$ . Aniline acts sometimes with explosive violence, producing acetamide and tribromaniline (m. p.  $117^\circ$ ); no nitrogen is evolved. Several other aromatic bodies act in a similar way, for example, phenol yields tribromophenol and acetamide.

When treated with strong soda-solution, acetomonobromamide forms a sodium salt which may remain for hours in the cold soda without decomposing. If, however, the solution is moderately diluted and carefully heated at  $60-70^\circ$ , until acids no longer produce a yellow coloration, sodium bromide and carbonate, and methylamine are produced. Methyl cyanate is likewise formed as an intermediate product, and if the monobromamide is mixed with silver carbonate, and gently warmed, the methyl cyanate is given off; but the reaction is very violent, so that it is necessary to moderate it by mixing the reagents with a neutral body, such as sand. This reaction renders the formation of methylacetocarbamide still clearer, for methyl cyanate and acetamide yield the carbamide.

Cold and moderately warm water are without action on acetomonobromamide. When, however, the two bodies are boiled together, brown vapours are given off, and acetamide and a small quantity of methyl-acetocarbamide are produced. The brown vapours are a mixture of bromine and hypobromous acid,  $\overline{\text{Ac}}\text{NHBr} + \text{H}_2\text{O} = \overline{\text{Ac}}\text{NH}_2 + \text{HBrO}$ ; and  $2\overline{\text{Ac}}\text{NHBr} = \text{NMeH.CO.N}\overline{\text{Ac}}\text{H} + \text{Br}_2$ . If a dilute solution of 1 mol. monobromamide is mixed with 1 mol. bromine, and saturated with potash, golden-yellow needles or leaflets of acetodibromamide separate

out. They can be crystallised at 100° from warm water without decomposition, are soluble in ether and alcohol, melt, when dry, and volatilise with partial decomposition at a higher temperature. Boiled with water the compound is converted successively into the monobromamide and acetamide. Hydrochloric acid changes it into acetomonochloramide. When treated with alkali, there is a violent evolution of gas, a hypobromite and acetamide being evidently formed, and the latter being changed into acetic acid and ammonia, which is decomposed by the hypobromous acid, with evolution of nitrogen. Ultimately the solution contains acetate and hypobromite, or if it has been heated, simply a bromate of the alkali. By admixture with acetamide in molecular proportion, pure acetomonobromamide is formed:  $\text{AcNBr}_2 + \text{AcNNH}_2 = 2\text{AcNHBr}$ .

If soda be used instead of potash in the preparation of acetomonobromamide, it must be used in dilute solutions only, and then the amide will remain in solution and will have to be extracted with ether. When concentrated soda is used, a body,  $\text{C}_2\text{H}_5\text{NaNO}_2\text{Br}_3$ , is formed thus:  $-\text{C}_2\text{H}_5\text{ONH}_2 + 2\text{Br}_2 = 2\text{NaHO} = \text{C}_2\text{H}_5\text{NaNO}_2\text{Br}_3 + \text{NaBr} + \text{H}_2\text{O}$ . It crystallises in yellow rectangular plates, which dissolve in water, the solution, however, soon deposits a mass of yellow crystals of dibromamide. It will be seen that the relative quantities of the materials used, and also the nature of the alkali employed, are of importance to the success of these experiments. D. A. L.

**Reduction-processes in the Animal Body.** By V. MERING (*Ber.*, 15, 1019—1021).—The author, in conjunction with Musculus, has shown that, after doses of chloral hydrate, the urine contains a lævorotatory acid which reduces cupric oxide, named *urochloralic acid*,  $\text{C}_7\text{H}_{12}\text{Cl}_2\text{O}_6$ , which on boiling with alkalis turns brown and gives an odour of caramel. Similar compounds have been found after introduction into the system of nitrobenzene and other aromatic compounds. The author finds that urochloralic acid has the formula  $\text{C}_8\text{H}_{11}\text{Cl}_3\text{O}_7$ , and is decomposed, on boiling with dilute acids, into trichlorethyl alcohol and glycuronic acid, thus:  $\text{C}_8\text{H}_{11}\text{Cl}_3\text{O}_7 + \text{H}_2\text{O} = \text{C}_2\text{H}_3\text{Cl}_3\text{O} + \text{C}_6\text{H}_{10}\text{O}_7$ . Similarly, after taking butylchloral hydrate, the urine contains an acid,  $\text{C}_{10}\text{H}_{15}\text{Cl}_3\text{O}_7$ , which on boiling with acids is decomposed into trichlorobutyl alcohol and glycuronic acid. The former substance crystallises in long prisms (m. p. 61°, b. p. 200°), converted by oxidation into trichlorobutyric acid. The trichlorethyl and trichlorobutyl alcohols are formed by reduction-processes in the animal organism.

V. H. V.

**Formula of Benzene.** By E. WROBLEWSKY (*Ber.*, 15, 1023).—The author remarks that Kekulé's formula does not account for the symmetrical pairs of hydrogen-atoms, the presence of which has been established by the author's experiments and those of Hübner and Petermann.

V. H. V.

**Synthesis of Aromatic Hydrocarbons.** By H. GOLDSCHMIDT (*Ber.*, 15, 1066—1068).—Aromatic ethers and homologues of aniline have been obtained by the action of zinc chloride on the phenols and mixtures of aniline and the paraffinoid alcohols. By a similar reaction



the author has obtained homologues of benzene by the action of zinc chloride on mixtures of benzene and its homologues with the paraffinoid alcohols. Thus, benzene and isobutyl alcohol give isobutylbenzene and dibutylbenzene; toluene and butyl alcohol give methylbutylbenzene, and benzene and ethyl alcohol give ethylbenzene, although in the latter case the yield was small, owing to difficulties of manipulation.

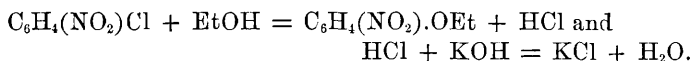
V. H. V.

**Action of Alcoholic Potash on Paranitrochlorobenzene.** By C. WILLGERODT (*Ber.*, **15**, 1002—1005).—The author has examined the action of potash, dissolved in various alcohols and under different conditions, on paranitrochlorobenzene, with the following results:—

(1.) Potash dissolved in absolute or high-percentage alcohol, at a temperature of 100—130°, reduces paranitrochlorobenzene to dichlorazoxybenzene, and at 150—200° to dichlorazobenzene.

(2.) The reducing power of the alcoholic solution varies with the alcohol used; thus, ethyl alcohol forms dichlorazoxybenzene at once, without assisting the reaction by the application of heat, while methyl alcohol has only a moderate reducing action, a considerable quantity of paranitranisole being formed in the reaction besides the dichlorazobenzene.

(3.) On diluting the alcohol with water, the reducing power is considerably modified, paranitrophenetol being obtained on heating paranitrochlorobenzene with dilute alcoholic potash, thus:—

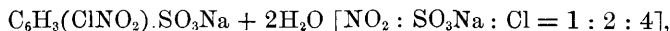


In order to separate the phenetol from the unaltered nitrochlorobenzene, and from any dichlorazoxybenzene which may be formed, the crude product is distilled in a current of steam, when the nitrophenetol passes over. Similarly, on substituting methyl for ethyl alcohol, paranitranisole is obtained.

(4.) Finally, by the action of more dilute alcoholic potash on paranitrochlorobenzene potassium nitrophenate is formed, either by the replacement of the chlorine-atom by the OK group, or by the saponification of the intermediate phenetol, or more probably by both of these reactions.

V. H. V.

**Orthodinitro.compounds.** By A. LAUBENHEIMER (*Ber.*, **15**, 597—599).—In former communications (*Ber.*, **9**, 768, 1826; and **11**, 1155) it has been shown that orthodinitro-compounds react with alkalis, ammonia, and compound ammonias, in such a way that one of the two nitro-groups is replaced by another atomic group, thus, orthodinitrobenzene gives orthonitrophenol when boiled with potash. This reaction is now extended to orthodinitrochlorobenzene [ $\text{NO}_2 : \text{NO}_2 : \text{Cl} = 1 : 2 : 4$ ] (m. p. 37.1°), which by the action of sodium sulphite is converted into *sodium nitrochlorobenzenesulphonate*,



crystallising from alcohol in brilliant thin prisms or needles, of pale reddish-yellow colour. On drying over sulphuric acid it loses

1 mol.  $\text{H}_2\text{O}$ , and the second at  $100-120^\circ$ . It dissolves in 15.8 parts of water at  $5.3^\circ$ ; and is less soluble in alcohol. Its concentrated solution is not precipitated by calcium chloride, lead acetate, silver nitrate, copper sulphate, or mercurous chloride, or mercurous nitrate, nor by barium chloride, except on long standing. *Nitrochlorobenzene sulphonamide*,  $\text{C}_6\text{H}_3(\text{ClNO}_2).\text{SO}_2\text{NH}_2$ , crystallises from alcohol in four-sided leaflets ( $158-159^\circ$ , uncorr.), and from water in needles; it is moderately soluble in alcohol, but less soluble in cold water.

T. C.

**Oxidation of Symmetrical Nitroxylenes.** By E. WROBLEWSKY (*Ber.*, 15, 1021—1023).—From a comparison of many researches the generalisation has been drawn, that when a halogen or nitro-derivative of benzene, with a side-chain, is oxidised with chromic acid, the side-chain the farthest removed from the halogen or nitro-group, is converted into the corresponding carboxyl-group. Beilstein and Kreusler have studied the oxidation of a nitroxylenes, which further experiments showed to be a mixture of three isomerides, containing the groupings  $\text{Me} : \text{Me} : \text{NH}_2$ , in the positions 1 : 3 : 4 and 1 : 4 : 5 and 1 : 2 : 4; but in these cases the methyl-group in the position 1 was oxidised, whilst the other was unattacked. The author has studied the oxidation of symmetrical nitroxylenes  $\text{Me} : \text{Me} : \text{NO}_2 = 1 : 3 : 5$ , containing both the methyl-groups in the same position relatively to the nitro-group, and has found that both the groups are oxidised, with formation of nitro-isophthalic acid. The result confirms the theory stated above.

V. H. V.

**Laws of Substitution of Aromatic Amines.** By C. LANGER (*Ber.*, 15, 1061—1065).—The author has made a series of generalisations and experiments on the laws of the substitution of the aromatic amines by the halogens.

As aniline forms directly trichlor- and tribromaniline, it would, *à priori*, be expected that monochloraniline would take up 2 atoms, and dichloraniline 1 atom of chlorine. This is the case if the chlorine-atoms occupy the ortho- or para-position to the amido-group; but in the case of the meta-derivatives the presence of the halogen does not diminish the number of atoms taken up, since the substituted amine takes up the same number of atoms as the amine itself. Thus metabromaniline, for example, forms tetrabromaniline, and the symmetrical dibromaniline  $[\text{NH}_2 : \text{Br} : \text{Br} = 1 : 3 : 5]$  forms pentabromaniline. To establish this generalisation, the author has studied the action of halogens on meta- and ortho-nitraniline and the three chloranilines. It is shown that metanitraniline forms trichlor-, but orthonitraniline dichlor-nitraniline; parachloraniline gives trichloraniline with orthochloraniline, bromine gives dibromochloraniline, but metachloraniline takes up 3 atoms of bromine to form tribromochloraniline.

Tribromochlorobenzene from tribromochloraniline crystallises in golden-yellow needles (m. p.  $82^\circ$ ), easily soluble in alcohol.

V. H. V.

**Action of Nitric Acid on Tribromaniline.** By S. M. LOSANTSCH (*Ber.*, 15, 471—474).—Snow-white tribromaniline (m. p.  $119^\circ$ ) is prepared by pouring a solution of bromine in aqueous alcohol into

aniline suspended in water. When tribromaniline is boiled with hot concentrated nitric acid, *dibromodinitromethane* distils over, and tetrabromobenzene remains in the flask together with *bromanil*, *oxalic acid*, and *picric acid*, and a dark red substance soluble in alcohol. Dibromodinitromethane,  $\text{CBr}_2(\text{NO}_2)_2$ , can be obtained pure by precipitation from its potassium derivative and distillation with steam; it forms a greenish-yellow mobile liquid having a suffocating odour; its vapour attacks the eyes. It solidifies at a few degrees above zero to a white crystalline mass, and at  $50^\circ$  begins to decompose, bromine distilling off; it volatilises with steam without decomposition. It is insoluble in water, but miscible in all proportions with alcohol. It does not burn in the air. It combines with basic hydrates, one bromine-atom being replaced by a metal, forming saline compounds. These bodies are yellow, and explode easily. The *potassium derivative*,  $\text{CKBr}(\text{NO}_2)_2$ , forms large pale-yellow brilliant crystals, easily soluble in warm water, less so in alcohol. The aqueous solution is decomposed by prolonged boiling, giving off an odour of dibromodinitromethane. Acids decompose it with separation of dibromonitromethane. This derivative explodes either by percussion or heating. The *sodium and ammonium derivatives* are similar to that of potassium; they are, however, easily soluble in alcohol. The *tetramethylammonium derivative* crystallises in feathery groups of yellow needles.

When nitric acid acts on tetrabromaniline in glacial acetic acid solution the same products are formed; if, however, the heating of the mixture be stopped when the red fumes begin to come off, then *dibromonitraniline*,  $\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)\text{NH}_2$ , is formed. It crystallises in brilliant sulphur-yellow needles (m. p.  $206-207^\circ$ ) soluble in boiling alcohol and in glacial acetic acid.

When the reaction with nitric acid and tetrabromaniline in glacial acetic acid solution is conducted in the presence of alcohol, and the mixture is boiled for some time, a white crystalline (needles, m. p.  $119-120^\circ$ ) sublimate of tribromobenzene,  $\text{C}_6\text{H}_3\text{Br}_3$ , is deposited.

D. A. L.

**Action of Carbon Bisulphide on Paranitraniline.** By S. M. LOSANITSCH (*Ber.*, **15**, 470—471).—Metanitraniline (m. p.  $110^\circ$ ) is converted into 1:3 dinitrodiphenylthiocarbamide by boiling in alkaline solution with carbon bisulphide. The author has tried an experiment with [1:4] nitraniline. When a strongly alkaline alcoholic solution of this substance and carbon bisulphide is boiled for a week in a flask with reflux condenser, the carbon bisulphide distilled off, and the residue acidified with hydrochloric acid and diluted, [1:4] *nitrophenylxanthamide*,  $\text{SEt.CO.NH.C}_6\text{H}_4\text{NO}_2$ , crystallises out in small yellow needles (m. p.  $175-176^\circ$ ), soluble in alcohol. In fact, thiourethanes (along with thiocarbamides) are always formed when aromatic amines are boiled for a long time with carbon disulphide in alkaline alcoholic solutions. In this way the author has prepared the respective thiourethanes from aniline, [1:4] chloraniline, and [1:4] toluidine.

D. A. L.

**Mesidine Derivatives.** By J. EISENBERG (*Ber.*, **15**, 1011—1019).—The author has prepared and examined several derivatives of mesi-

dine. On heating mesidine with twice its weight of carbon disulphide with addition of alkali and alcohol, *mesitylthiocarbimide* is formed, which crystallises in long glistening needles (m. p.  $64^{\circ}$ ), soluble in alcohol, ether, and benzene. If mesidine and carbon bisulphide are heated in molecular proportion without addition of alkali, *dimesitylthiocarbimide*,  $\text{CS}(\text{NH}.\text{C}_6\text{H}_2\text{Me}_3)_2$ , crystallising in white needles (m. p.  $196^{\circ}$ ), is obtained.

*Mesitylthiocarbimide*,  $\text{NH}_2.\text{CS}.\text{NHC}_6\text{H}_2\text{Me}_3$ , is best prepared by warming mesitylthiocarbimide with alcoholic ammonia; it crystallises in glistening leaflets (m. p.  $222^{\circ}$ ), easily soluble in ether, insoluble in water; it forms a well-crystallised platinochloride. Similarly mesitylphenyl- and orthotolylthiocarbimides can be obtained. By the action of lead oxide on dimesitylthiocarbimide in presence of ammonia, *dimesitylguanidine*,  $\text{CNH}(\text{NH}.\text{C}_6\text{H}_2\text{Me}_3)_2$ , is obtained, crystallising in small prisms (m. p.  $218^{\circ}$ ) insoluble in water, soluble in alcohol and benzene: it is a monoacid base; on substituting mesidine for ammonia in the reaction above, *trimesitylguanidine* is formed.

On digesting mesitylthiocarbimide with ethyl alcohol, mesitylethylthioic acid,  $\text{C}_6\text{H}_2\text{Me}_3\text{NC}(\text{SH})\text{OEt}$ , is formed, crystallising in delicate needles (m. p.  $88^{\circ}$ ), soluble in alcohol, ether, soda, and baryta solutions; it forms a hydrochloride, and mercury, copper, lead, and silver salts.

By the action of ethyl chlorocarbonate on mesidine, besides mesidine hydrochloride, there is formed *mesityl-ethyl carbonate*,



crystallising in long colourless needles melting at  $61^{\circ}$ ; on distillation it decomposes, with formation of *mesitylcarbimide*. This latter compound is best obtained by distilling the carbonate with phosphoric anhydride; it is a colourless, disagreeably smelling liquid (b. p.  $218^{\circ}$ ), which on standing decomposes and deposits a white, gelatinous mass: it combines directly with ammonia and the amines to form substituted carbamides; with mesidine it gives *dimesitylcarbimide*,  $\text{CO}(\text{NH}.\text{C}_6\text{H}_2\text{Me}_3)_2$ , crystallising in delicate prisms melting at  $300^{\circ}$ .

On heating mesidine with phthalic anhydride, mesitylphthalimide,  $\text{C}_6\text{H}_4:\text{C}_2\text{O}_2:\text{N}.\text{C}_6\text{H}_2\text{Me}_3$ , is formed, crystallising in long silky needles (m. p.  $171^{\circ}$ ), insoluble in water, easily soluble in alcohol, ether, &c. Mesitylphthalimide gives with fuming nitric acid a mononitro-derivative, crystallising in golden prisms (m. p.  $210^{\circ}$ ), decomposed on boiling with alcoholic potash, with formation of nitromesidine. With a mixture of nitric and sulphuric acids, mesitylphthalimide gives a dinitro-compound (m. p.  $242^{\circ}$ ) crystallising in long spike-shaped crystals, insoluble in water, soluble in alcohol and acetic acid.

Mesidine when heated with succinic acid gives mesityl succinimide, crystallising in pearly leaflets (m. p.  $137^{\circ}$ ), easily soluble in alcohol and acetic acid.

Further researches on mesidine-derivatives are promised.

V. H. V.

**Compounds of Benzotrichloride with Aromatic Bases.** By O. DOEBNER (*Ber.*, 15, 232—239).—The action of benzotrichloride on aniline gives rise to two different products according as the reaction is

so conducted as to lead to the replacement of the hydrogen of the amido-group or of the benzene nucleus. By gently heating together benzotrichloride and aniline, the *benzoyldiphenylamidine* of Limpricht (*benzoyldiphenyldiamine*)  $\text{CPh}(\text{NHPH}) : \text{NPh}$  is obtained; it crystallises from alcohol in long needles (m. p.  $144^\circ$ ), the *platinochloride*,  $(\text{C}_{19}\text{H}_{16}\text{N}_2, \text{HCl})_2, \text{PtCl}_4$ , crystallises in small yellow needles, the *picrate*,  $\text{C}_{19}\text{H}_{16}\text{N}_2, \text{C}_6\text{H}_3\text{N}_3\text{O}_7$ , in yellow needles. On heating the base with concentrated hydrochloric acid at  $150^\circ$ , it is decomposed into benzoic acid and aniline.

*Diamidotriphenylcarbinol*,  $\text{CPh}(\text{C}_6\text{H}_4.\text{NH}_2)_2.\text{OH}$ , the product resulting from substitution in the benzene nucleus, is best obtained by heating aniline hydrochloride (40 parts), nitrobenzene (45 parts), benzotrichloride (40 parts), and iron filings (5 parts) in a vessel provided with a reflux condenser for 3—4 hours at  $180^\circ$ . The hydrochloride,  $\text{C}_{19}\text{H}_{16}\text{N}_2.\text{HCl}$ , thus produced forms small dark-blue crystals moderately soluble in cold, more readily in hot water, readily soluble in alcohol and glacial acetic acid; the solutions have a red-violet to violet colour, and dye silk bluish-violet. On addition of an alkali, the free base is precipitated, and can be obtained from its alcoholic solution in small indistinct pale yellow crystals. It melts below  $100^\circ$  to a bluish-violet oil, and can be heated to  $130^\circ$  without decomposition; it is insoluble in water, readily soluble in alcohol and benzene. Dilute acids dissolve it in the cold to violet solutions; concentrated acids decolorise the solutions. The basic properties are not strongly marked, boiling with water causing a partial dissociation of the salts.

On boiling a solution of the hydrochloride with zinc, it is reduced to diamidotriphenylmethane. By heating it with excess of methyl iodide for some hours at  $120^\circ$ , malachite-green is formed. Aniline hydrochloride at  $180$ — $200^\circ$ , converts it into a bluish-green dye, in all probability  $\text{CPh}(\text{C}_6\text{H}_4.\text{NHPH})_2.\text{OH}$ .

Diamidotriphenylcarbinol can also be prepared from benzoylanilide,  $\text{Ph.CO.C}_6\text{H}_4.\text{NH}_2$ , by heating it with phosphoric chloride, and mixing the resulting chloride ( $\text{Ph.CCl.C}_6\text{H}_4$ ?) with aniline and con-



centrated sulphuric acid. As benzoylanilide belongs to the para series, it follows that at least one amido-group must be in the para position relatively to the methane carbon-atom, and it is very probable that both amido-groups are para, as O. Fischer has shown that diamidotriphenylmethane is converted by nitrous acid into the dihydroxytriphenylmethane that can be prepared from benzotrichloride and phenol.

A. J. G.

**Action of Ethyl Chloracetate on Phenylenediamine.** By J. ZIMMERMANN (*Ber.*, 15, 518—519).—When 2 mols. ethyl monochloracetate are gently warmed with 2 mols. phenylenediamine, a violent action soon sets in, accompanied by great development of heat. The ethereal extract of the product deposits on evaporation crystals of *ethyl meta-phenylenediglycocolate*,  $\text{C}_6\text{H}_4[\text{NH} : \text{CH}_2.\text{COOEt}]_2$ , which forms fine needles (m. p.  $73^\circ$ ) very sparingly soluble in water, easily in alcohol and ether. Toluylenediamine reacts in an analogous manner, but the product has not yet been examined.

D. A. L.

**Formation of Bases from Acid Amides.** By C. WALLACH (*Ber.*, **15**, 208—211).—Formanilide when treated at 100° with gaseous hydrochloric acid, yields methenyldiphenyldiamine. Acetanilide similarly treated at 150° gives ethenyldiphenyldiamine. Equal weights of acetamide and aniline hydrochloride heated together also yield ethenyldiphenyldiamine, the yield being so considerable as to make this the best method of preparing the base. A. J. G.

**Action of Heat on Thioformanilide.** By W. W. J. NICOLL (*Ber.*, **15**, 211—212).—On heating thioformanilide in sealed tubes at 180° for 6—7 hours, hydrogen sulphide is obtained, together with a substance,  $C_{14}H_{12}SN_2$ , crystallising in scales and plates melting at 140°, readily soluble in alcohol, nearly insoluble in hot benzene; when treated with a hot soda-solution, it first dissolves and then decomposes into aniline, formic acid and hydrogen sulphide. The platino-chloride,  $C_{14}H_{12}N_2S \cdot 2HCl \cdot PtCl_4$ , does not crystallise. A. J. G.

**Behaviour of Dimethylphenylphosphine with Ethylene Bromide.** By L. GLEICHMANN (*Ber.*, **15**, 198—200).—On mixing equal molecular weights of ethylene bromide and dimethylphenylphosphine, the whole solidifies to a crystalline mass of *bromethyldimethylphenylphosphonium bromide*,  $PMe_2Ph(C_2H_4Br)Br$ . It crystallises in colourless tables (m. p. 187°), readily soluble in hot alcohol and water; 100 parts of alcohol at 18° dissolve 35.4 parts of the salt. Silver nitrate precipitates one-half of the bromine from its solution, whilst silver oxide removes the whole. With platinic chloride it yields a yellowish-red crystalline powder,  $[PMe_2Ph(C_2H_4Br)Br]_2 \cdot PtCl_4$ . It can also unite with 2 mols. of bromine, giving a red crystalline powder, from which the added bromine can be again removed by heating in air.

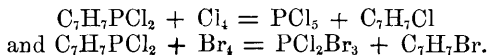
By heating the foregoing compound in concentrated alcoholic solution with a further quantity of dimethylphenylphosphine, a crystalline precipitate of the composition  $C_2H_4(PMe_2PhBr)_2$ , is obtained. It dissolves in 50 parts of alcohol at 21°, melts above 300°, and gives with platinic chloride a deep red precipitate insoluble in water. The whole of the bromine can be removed by silver nitrate. The salt can combine with 5 mols. of bromine, forming a red powder. On dissolving this in hot glacial acetic acid, bromine is eliminated, and on cooling, a yellow crystalline compound,  $C_2H_4(PMe_2PhBr)_2 \cdot Br_2$ , is obtained (m. p. 171°). A. J. G.

**Homologues of Phosphenyl Chlorides.** By A. MICHAELIS and C. PANECK (*Annalen*, **212**, 203—239).—These compounds are prepared by heating toluene and its higher homologues with phosphorous chloride and aluminium chloride.

**I. TOLYLPHOSPHO-COMPOUNDS.**—Toluene (150 g.), phosphorous chloride (200 g.), and aluminium chloride (30 g.) are heated in a flask with reversed condenser, placed in a sand-bath over a small flame. At first hydrogen chloride is abundantly evolved, but this soon ceases, and the liquid usually separates into two layers. It is then treated with twice its volume of toluene, 1—1.5 c.c. water is added, and the whole is

warmed for a short time, after which the liquid is poured into a tap-funnel, and left to clarify from 24—36 hours, and the resinous oil which separates is removed and distilled, passing over below 120°. The residue is again mixed with a quantity of toluene sufficient to produce strong turbidity, and once more left to stand in the tap-funnel, till it becomes clear, which takes place in 12—18 hours. The sediment is then removed, the greater part of the toluene distilled off at about 130°, and the residue finally submitted to fractional distillation in a stream of carbonic anhydride.

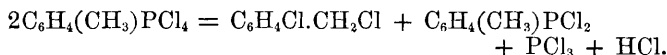
*Tolylphosphochlorides*.—In this manner two portions of liquid were obtained, one of which, after removal of admixed toluene, boiled at 236—240°, the other at 240—250°. These liquids, exposed to the temperature of a mixture of snow and salt, solidified to a laminar mass drenched with an oily liquid, and on removing this liquid by straining and pressure, remelting the remaining crystals, again solidifying them, and repeating the whole of this treatment several times, two portions were obtained, one melting at 25°, while the other required a very low temperature to solidify it, and was found to consist of a mixture of the solid chloride with a small portion of a lower-boiling hydrocarbon, and perhaps also of a liquid phosphochloride. Both the solid and the liquid chlorides give by analysis numbers agreeing with the formula  $C_7H_7PCl_2$ . Moreover the solid phosphochloride was found to agree in melting point and properties with that which is obtained by the action of  $PCl_3$  on mercury-ditolyl: hence it consists of *paratolylphosphodichloride*,  $C_6H_4(CH_3)PCl_2$ . This chloride forms a colourless mass of long needles, melting at 25° and boiling at 245°. It fumes slightly in the air, more strongly in the fused state; dissolves readily in ether, chloroform, benzene, and carbon sulphide, behaving indeed in every respect like phenylphosphodichloride. With water and with alcohol it reacts violently, yielding *tolylphosphinic acid*,  $C_7H_7PO_2H_2$ , together with  $HCl$  and  $C_2H_5Cl$  respectively. It takes up chlorine and bromine, with great evolution of heat, and is resolved by an excess of either of these halogens into phosphoric chloride or chlorobromide and chloro- or bromotoluene:



*Orthotolylphosphodichloride*,  $C_6H_4(CH_3)PCl_2$ , obtained by the action of phosphorous chloride on mercury-ditolyl (m. p. 107°), is a colourless liquid, which does not solidify at -20°, becomes yellowish and turbid on exposure to the air, and boils constantly at 244°. In its other properties and in its reactions it exactly resembles the para-compound.

*Tolylphosphotetrachlorides*,  $C_6H_4(CH_3)PCl_4$ , *p*- and *o*-, are formed by passing dry chlorine gas into the corresponding dichlorides contained in cooled vessels. The *para*-compound is a very hard light yellow mass, somewhat like phosphorus pentachloride, easily soluble in dry benzene, and separating from the concentrated solution in acuminate prisms. It melts at 42°, and absorbs moisture greedily from the air, deliquescing and being converted into *p*-tolylphosphoroychloride,  $C_7H_7POCl_2$ . With water it forms at first the oxychloride, which, however, is quickly con-

verted into tolylphosphinic acid,  $C_7H_7PCl_4 + H_2O = 2HCl + C_7H_7POCl_2$ ; and  $C_7H_7POCl_2 + 2H_2O = 2HCl + C_7H_7P(OH)_2$ . With dry *sulphurous oxide* the tetrachloride likewise deliquesces, yielding thionyl chloride and tolylphosphoroxychloride,  $C_7H_7PCl_4 + SO_2 = SOCl_2 + C_7H_7POCl_2$ .—The tetrachloride heated in an open tube is partly resolved into free chlorine and the dichloride, but when heated in sealed tubes at  $200^\circ$ , it suffers more complete decomposition, being resolved into parachlorobenzyl chloride, paratolylphosphochloride, phosphorus trichloride, and hydrogen chloride:



The phosphodichloride also takes up *bromine*, with rise of temperature, and solidifies therewith to a flesh-coloured mass, which, when treated with excess of bromine, is resolved with a hissing noise into a bromotoluene and a haloid compound of phosphorus.

*Orthotolylphosphotetrachloride*,  $C_6H_4(CH_3)PCl_4$ , is a yellow solid body, prepared like the *p*-compound, and exhibiting similar reactions. The quantity of it obtained was too small for complete investigation. The differences between the two isomerides are best seen in their acid derivatives.

*Paratolylphosphoroxychloride*,  $C_6H_4(CH_3)POCl_2$ , is best obtained by the action of dry sulphurous oxide on *p*-tolylphosphotetrachloride:  $C_6H_4MePCl_4 + SO_2 = SOCl_2 + C_6H_4MePOCl_2$ . It is also formed, as above stated, by treating the tetrachloride with a small quantity of water. It is a nearly colourless viscid liquid, which boils at  $284$ — $285^\circ$ , and is rapidly decomposed by water into hydrochloric and tolylphosphinic acids.

The above described tolylphosphochlorides, when decomposed by water, also yield acids, one of which is analogous to phosphorous, the other to tribasic phosphoric acid, compounds in which the differences between the ortho- and para-modifications come out more distinctly than in the chlorides.

*Tolylphosphinous acids*.—The *para*-acid,  $C_6H_4Me.PO_2H_2$ , analogous to phosphorous acid, is easily prepared by the action of water on *p*-tolylphosphodichloride. It is but very slightly soluble in water, even when warm, and separates at the bottom of the vessel as a thick oil, which solidifies on cooling; and on decanting the supernatant liquid, washing the solidified residue repeatedly with cold water to remove hydrochloric acid, then dissolving it in alcohol, and leaving the filtrate to evaporate over sulphuric acid, the tolylphosphinous acid separates in transparent, colourless, nearly square plates, melting at  $104$ — $105^\circ$ . It is nearly insoluble in cold water acidulated with hydrochloric acid, but dissolves readily in alcohol, less readily in ether. It is but little altered by exposure to the air. When boiled with nitric acid it is oxidised, with partial nitration, to paratolylphosphinic acid. The same product is formed by the action of moist chlorine, part of it, however, undergoing further oxidation. Paratolylphosphinous acid is resolved by



heat, just like phosphorous acid, into tolylphosphine and paratolylphosphinic acid.

Paratolylphosphinous acid is monobasic. The *potassium salt*,  $C_7H_7POHK$ , prepared by neutralising the alcoholic solution of the acid with potash, crystallises in tufts of slender nacreous needles.— $C_7H_7PO_2H(NH_4)$  forms white silky laminæ, soluble in water and in alcohol, moderately permanent in the air.— $(C_7H_7PO_2H)_2Ba$  forms white crystalline laminæ.  $(C_7H_7PO_2H)_2Pb$  is obtained by mixing the sodium salt with lead acetate, as a crystalline precipitate, and the mother-liquor yields an additional quantity in nacreous scales.— $(C_7H_7PO_2H)Cu + 4H_2O$  is obtained by precipitation in thin shining laminæ, and in needles on mixing its very dilute aqueous solution with an equal volume of alcohol.—The *ethyl salt*,  $C_7H_7P(OEt)_2$ , produced by the action of *p*-tolylphosphochloride on dry sodium ethylate free from alcohol, with addition of anhydrous ether to mitigate the violence of the reaction, as a thick transparent liquid, which distils at  $280^\circ$ , and does not solidify on cooling. It bleaches corks, and has a disagreeable and extremely persistent odour. Water resolves it into alcohol and tolylphosphorous acid.

*Reactions of Sodium p-Tolylphosphinite*.—With  $CaCl_2$ , no precipitate; slight on addition of ammonia.— $BaCl_2$ , no precipitate.— $CuSO_4$ , in aqueous solution, precipitate of faintly blue shining laminæ, partly dissolving on boiling, and disappearing altogether on addition of alcohol; solution deposits the  $Cu$ -salt in small shining needles.— $AgNO_3$ , white flocculent precipitate, soluble in nitric acid.— $Fe_2Cl_6$ , light yellow precipitate, soluble in a large quantity of cold concentrated hydrochloric acid.— $CO(NO_3)_2$ , precipitate of rose-coloured laminæ, formed only at boiling heat, and soluble in acids.— $NiCl_2$ , faintly green granular precipitate, formed on boiling, and soluble in acids.— $Pb(\overline{AcO})_2$ , white crystalline precipitate, somewhat soluble on boiling, and crystallising from the solution in large laminæ.— $HgCl_2$ , white crystalline precipitate at boiling heat, turning grey on further boiling, or on addition of hydrochloric acid.— $MnCl_2$ : in strong solution of sodium salt there is gradually formed a crystalline precipitate, which dissolves in hydrochloric acid.

*Orthotolylphosphinous acid*,  $C_6H_4(CH_3)^1.P\overset{2}{O}_2H_2$ , is obtained by decomposing the corresponding chloride with water, as a thick heavy oil. It dissolves readily in ammonia and in alcohol, but shows no disposition to crystallise, even after repeated purification. Its lead and copper salts also do not appear to crystallise. The *barium salt* crystallises in needles from a solution of the ammonium salt mixed with barium chloride. The *calcium salt* is obtained in like manner in brilliant laminæ; easily soluble in water, and having the composition  $(C_7H_7PO_2H)Ca + H_2O$ .—The acid gives a yellow precipitate with *ferric chloride*, white with *silver nitrate*.

*Tolylphosphinic acids*,  $C_6H_4(CH_3)PO(OH)_2$ .—The *para*-acid is prepared by slowly adding tolylphosphotetrachloride, free from adhering chlorine, to cold water, whereupon it is first converted into the oxychloride, which sinks to the bottom as a heavy oil, and then into the phosphinic acid, which dissolves slowly in the cold, more quickly on

boiling. This acid crystallises in felted tufts of slender needles, which may be freed from adhering mother-liquor and hydrochloric acid by repeated crystallisation, and drying in a vacuum over soda-lime. It is also formed by the action of water on *p*-tolylphosphochlorobromide and -oxychloride, and, as a secondary product mixed with metaphosphoric acid, in the preparation of *p*-tolylphosphine from *p*-tolylphosphinous acid, forming a glassy residue, the solution of which in water immediately deposits crystals of pure *p*-tolylphosphinic acid.—The paratolylphosphochlorides, prepared by different methods, yield one and the same *p*-tolylphosphinic acid.

This acid crystallises from water, as already observed, in felted woolly tufts of needles, having but little lustre. It dissolves readily in alcohol and ether, and crystallises therefrom in needles, having a strong silky lustre. It melts at 189°. It is a strong bibasic acid, and forms three series of salts, hyperacid, acid, and normal. It is decomposed by aqueous chlorine or bromine, being converted by the latter into monobromotoluene and phosphoric acid. By ignition with soda-lime it yields toluene and phosphoric acid:  $C_7H_7PO(OH)_2 + HOH = C_7H_8 + PO(OH)_3$ .

*Hyperacid potassium paratolylphosphinate* is formed on adding to a solution of the free acid neutralised with potash a further quantity of the free acid, till a thick precipitate is formed, converting the entire liquid into a semisolid mass. This precipitate dissolves on boiling, and the solution on cooling deposits the salt in shining colourless needles. It dissolves in a large quantity of water even in the cold, but is insoluble in alcohol, which throws it down from the aqueous solution in nacreous laminæ. The formation of this salt is characteristic of the acid, a cold concentrated solution of which, added to a moderately strong solution of the nitrate or other salt of potassium, immediately forms a crystalline precipitate, especially if the surface of the tube be rubbed with a glass rod. The precipitate dissolves on heating, and separates on cooling in shining needles.

*Acid barium p-tolylphosphinate*,  $(C_7H_7PO.OH.O)_2Ba$ , is obtained by adding barium chloride to a solution of the acid neutralised with potash, as a shining crystalline precipitate, very slightly soluble in water, quite insoluble in alcohol.

*Acid silver paratolylphosphinate*,  $C_7H_7PO_2OHAg$ , is a white precipitate composed of shining laminæ, dissolving in the mother-liquor and in water on boiling; very slightly soluble in alcohol.—The *normal salt*,  $C_7H_7PO(OAg)_2$ , precipitated by silver nitrate from a neutral solution of the acid in ammonia, is white, curdy, darkens quickly on exposure to light, and dissolves in nitric acid, sparingly in water.

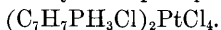
*Reactions of Potassium Paratolylsulphinate*.—With *copper sulphate*, a light blue precipitate; with *barium chloride*, white crystalline precipitate, soluble in acetic acid; with *calcium chloride* and *sulphate*, white crystalline precipitate, insoluble in alcohol, slightly soluble in boiling water; with *strontium chloride*, white crystalline, soluble in a large quantity of water; with *nickel sulphate*, apple-green precipitate; with *cobalt nitrate*, peachblossom-coloured granular precipitate, formed immediately at boiling heat, gradually at ordinary temperature; with *zinc sulphate*, white gelatinous precipitate; with *manganous chloride*,

white; with *cadmium chloride*, white finely flocculent precipitate; with *silver nitrate*, white curdy precipitate, blackening on exposure to light; with *molybdic acid*, no precipitate. The characteristic reaction of the free acid, as already observed, is that which it gives with potassium salts.

The acid treated in aqueous solution with a slight excess of *bromine* is resolved into *p*-bromotoluene and phosphoric acid:  $C_7H_7PO(OH)_2 + Br_2 + H_2O = C_7H_7Br + PO(OH)_3 + HBr$ . By oxidation with potassium permanganate in alkaline solution, it is converted into benzophosphinic acid,  $CO_2H.C_6H_4.PO(OH)_2$  (this Journal, 1881, Abstr., 603).

*Orthotolylphosphinic acid*, prepared like the para-compound from the *o*-tetrachloride, forms small granular crystals, melting at  $141^\circ$ , easily soluble in water, alcohol, and ether. The solution of its potassium salt gives with silver nitrate a white precipitate; with ferric chloride, a faint yellow precipitate, soluble in strong hydrochloric acid; with calcium chloride, a granular precipitate; with barium chloride, the same, but only after addition of a little alcohol. The acid does not exhibit the property characteristic of the para-modification (p. 962), of forming a sparingly soluble hyperacid potassium salt.

*Paratolylphosphine*,  $C_6H_4Me.PH_2$ , obtained by dry distillation of *p*-tolylphosphinous acid, is a liquid boiling at  $178^\circ$ , and solidifying at  $-7^\circ$  to a crystalline mass, which melts at  $+4^\circ$ . It has a fearful odour (like that of phenylphosphine), and produces headache and bleeding from the nose. In contact with the air it oxidises rapidly, with great rise of temperature, producing *p*-tolylphosphinous acid,  $C_7H_7MeP(OH)_2$ . In many of its properties it closely resembles Hofmann's benzylphosphine,  $CH_2(C_6H_5).PH_2$  (this Journal, 25, 422). It is insoluble in strong hydrochloric acid, but the mixture of the two yields with platinic chloride a yellow precipitate of the salt



Aqueous hydriodic acid, of sp. gr. 1.7, converts the phosphine into *p*-tolylphosphonium iodide,  $C_7H_7PH_3I$ , which when heated in an atmosphere of carbon dioxide at  $340^\circ$ , sublimes in cubes, and partly fuses. It absorbs water rapidly from the air, forming HI and tolylphosphine.

II. XYLYLPHOSPHO-COMPOUNDS.—The *dichloride*,  $C_8H_9PCl_2$ , was prepared by heating xylene (150 g.), phosphorous chloride (260 g.), and aluminium chloride (30 g.), in a reflux apparatus for 36 hours. Hydrogen chloride was then evolved, and the contents of the flask separated into two layers, which were separated in the manner described for the tolyl-compound, whereby 15 to 30 g. of high-boiling product was obtained; and this, when fractionally distilled in a stream of carbonic anhydride, yielded a portion boiling at  $260-290^\circ$ , and containing the xylyl-phosphochloride mixed with large quantities of condensed hydrocarbons, which it was found impossible to remove. The impure product, nevertheless, exhibited the characters of an aromatic phosphodichloride, being rapidly decomposed by water, with formation of hydrochloric and xylylphosphinous acid, and converted by assumption

of chlorine into a yellow crystalline pulp, containing xylylphosphotetrachloride, which when separated formed a light yellow liquid, turbid from separated phosphorus, remaining fluid at  $-18^{\circ}$ , and boiling at about  $270^{\circ}$ .

*Xylylphosphinous acid*,  $C_8H_9P(OH)_2$ , is obtained by decomposing the dichloride with water, as a heavy dark-coloured non-solidifying oil, somewhat contaminated with free xylene. It dissolves in a small quantity of alcohol, and the solution solidifies in the exsiccator to a pulp of crystals easily freed from the hydrocarbon by washing with ether, the acid then remaining as a fine white powder, which may be further purified by two crystallisations from alcohol, whereby it is obtained in flat colourless needles melting between  $97^{\circ}$  and  $98^{\circ}$ .

*Xylylphosphinic acid*,  $C_8H_9PO(OH)_2$ , obtained by the action of water on the tetrachloride, is easily soluble in water, alcohol, and ether, and crystallises in white slender needles melting at  $186-187^{\circ}$ .

Cymene, heated with  $PCl_3$  and  $AlCl_3$ , yielded a high-boiling product, which, after redistillation, boiled at about  $300^{\circ}$ , and remained liquid on cooling. It was apparently a mixture of condensed hydrocarbons with *cymylphosphodichloride*, as it took up chlorine when heated therewith, yielding a pasty mass interspersed with crystals, which was decomposed by water, with hissing and evolution of hydrochloric acid. The cymylphosphinic acid thus formed was, however, too small in quantity, and too much contaminated with other substances to admit of purification.

H. W.

**Homologous and Isomeric Rosanilines.** By A. ROSENSTIEHL and M. GERBER (*Compt. rend.*, **94**, 1319—1321).—When a mixture of 1 mol.  $\alpha$ -metaxylidine with 2 mols. aniline is oxidised with arsenic acid, a rosaniline is obtained which contains 20 atoms of carbon and is identical with that obtained by the oxidation of a mixture of aniline with the two toluidines. The melting and boiling points of the corresponding hydrocarbon are the same as those of the triphenylmethane obtained by E. and O. Fischer from commercial rosaniline.

*Toluene red*, first prepared by Coupier by oxidation of a mixture of 2 mols. ortho- and 1 mol. para-toluidine, consists mainly of a rosaniline which is very difficult to isolate in a state of purity. The corresponding hydrocarbon is also very difficult to isolate. It melts at  $36-40^{\circ}$ , and boils between  $360^{\circ}$  and  $363^{\circ}$ . The leucaniline crystallises easily from its ethereal solution, and melts at  $137^{\circ}$ . It is identical with the body obtained by the action of paranitrobenzaldehyde on 2 mols. orthotoluidine hydrochloride in presence of zinc chloride, with subsequent reduction by means of hydrochloric acid and tin. Toluene red contains a rosaniline which contains 21 carbon-atoms, and is the third term of the series. Starting from this term isomerism is possible, and the number of rosanilines is thus much increased. An isomeride of the preceding rosaniline is obtained by the action of arsenic acid on a mixture of amido-trimethylbenzene and aniline.

A fifth rosaniline, the fourth term of the series, containing 22 carbon-atoms, is obtained by oxidation of 1 mol.  $\alpha$ -metaxylidine and 2 mols. orthotoluidine. The corresponding hydrocarbon, tricesylmethane,

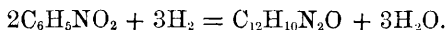
$C_{22}H_{22}$ , crystallises well from its solution in methyl alcohol. It melts at  $75^{\circ}$  and boils at  $377^{\circ}$ .

A sixth rosaniline is obtained by the oxidation of  $\alpha$ -metaxylylidine and 2 mols.  $\gamma$ -metaxylylidine. The corresponding hydrocarbon was not prepared, but it probably contains 24 carbon-atoms. This compound is not identical with the *xylene red*, which Coupier obtained by oxidation of xylylidine from coal-tar xylene.

In this series of compounds the difference between two consecutive terms is only slight. Generally, as the molecule becomes more complex, the hydrochloride becomes more soluble in water, crystallises with greater difficulty, and dyes wool a violet-red which approaches more and more to violet. The base becomes more soluble in ether, the boiling point of the corresponding hydrocarbon rises, and substitution becomes more difficult. The action of aniline, which with the first terms produces the well-known blues, becomes less marked, and the products dye only a violet-blue. C. H. B.

**Crystalline form of Azobenzene.** By P. ALEXEJEFF (*Jour. Russ. Chem. Soc.*, 1882, 198).—The author directs attention to the fact that azobenzene is still wrongly regarded as being monoclinic, though it has been shown by Jeremejeff, who determined the form of a sample prepared by the author, that azobenzene crystallises in forms of the rhombic system. Armascheffsky's new measurement on fresh crystals confirmed this conclusion. This is further confirmed by the circumstance that azoxybenzene, according to Bodewig, and azotoluene, according to Armascheffsky,—compounds which are closely related to azobenzene,—crystallise in the rhombic system. B. B.

**Azoxybenzene.** By N. MOLTCHANOFFSKY (*Jour. Russ. Chem. Soc.*, 1882, 224—226).—According to Schultz and Schmidt (*Annalen*, 207, 325) hydrazobenzene can be obtained from azoxybenzene only in small quantities. In order to prepare azoxybenzene, the author prefers Zimin's original method to its modification by Schultz and Schmidt, as the former yields 60 per cent. of the theoretical quantity of azobenzene, whereas on application of the modified method only 50 per cent. could be obtained by Schultz and Schmidt. The best method for the preparation of azoxybenzene is that proposed by Alexejeff in his "Monograph of Azo-compounds," viz., reduction of nitrobenzene by sodium amalgam (containing 3.8 per cent. of sodium) in alcoholic solutions, according to the equation:—



The yield was over 87 per cent. of the theoretical. It is advisable not to add acetic acid. On reducing azoxybenzene by sodium-amalgam, 76 per cent. of the theoretical amount of hydroazobenzene was obtained.

In order to save time, the author prefers to prepare hydroazobenzene directly from nitrobenzene by the action of sodium amalgam. At the ordinary temperature sulphide of ammonium is almost without action on azoxybenzene. Instead of sodium amalgam zinc-dust may be used as the reducing agent.

The small yield obtained by Schultz and Schmidt is explained by the circumstance that the reducing agent used by them, viz., tin and hydrochloric acid, was much too powerful, or that they used sulphide of ammonium, which does not act at ordinary temperatures.

According to the determinations made by the author, 100 parts of a solution of either of the three bodies in question in absolute alcohol, saturated at 16°, contains 17·5 parts of azoxybenzene, 8·5 parts of azobenzene, and 5 parts of hydroazobenzene.

B. B.

**Normal Dithiourethanes.** By A. BERNTHSEN and G. FRIESE (*Ber.*, 15, 563—572).—By the following series of reactions the authors have succeeded in obtaining a dithiourethane in which all the hydrogen has been replaced by alkyl radicles:—

- (1.)  $\text{CS}(\text{NPh})_2 + \text{EtI} = \text{NPh}:\text{C}(\text{NPh})\cdot\text{SEt} + \text{HI}$ .
- (2.)  $\text{NPh}:\text{C}(\text{NPh})\cdot\text{SEt} + \text{EtI} = \text{NPh}:\text{C}(\text{NEtPh})\cdot\text{SEt} + \text{HI}$ .
- (3.)  $\text{NPh}:\text{C}(\text{NEtPh})\cdot\text{SEt} + \text{CS}_2 = \text{CS}(\text{NEtPh})\cdot\text{SEt} + \text{PhNCS}$ .

*Phenylimidophenylcarbaminthiethyl*,  $\text{NPh}:\text{C}(\text{NPh})\cdot\text{SEt}$ , which has previously been described (*Ber.*, 14, 1774), forms a hydriodide, consisting of white crystals which melt at 157·5° after drying at 70°. Its aqueous solution is precipitated by soda; and on heating with aniline it gives mercaptan and triphenylguanidine. The hydriodide of *phenylimidoethylphenylcarbaminthiethyl*,  $\text{NPh}:\text{C}(\text{NEtPh})\cdot\text{SEt}$ , obtained by heating the preceding base with ethyl iodide at 120—150°, is a brown oil which after several days becomes crystalline. This salt is only sparingly soluble in hot water, but more soluble in water containing hydrochloric acid; the free base is precipitated from this solution by ammonia as a colourless oil, which apparently distils without decomposition. It is only a weak base, as both the hydrochloride and hydriodide undergo partial decomposition into free acid and free base when boiled with water. It forms an almost flesh-coloured platinochloride, which is insoluble in water, but readily soluble in alcohol; and melts at 110°.

*Ethylphenyldithiurethane*,  $\text{CS}(\text{NEtPh})\cdot\text{SEt}$ , is the first representative of a normal thiurethane in which all the hydrogen has been replaced by alkyl radicles. It is readily obtained from the above imido-carbaminthioether by heating with carbon bisulphide at 130—150°. It crystallises from alcohol in long snow-white prisms (m. p. 68·4—68·5 uncorr.; b. p. 305—315°, with partial decomposition), which are easily soluble in ether, chloroform, benzene, and glacial acetic acid, and hot alcohol, but only sparingly soluble in cold alcohol, and insoluble in water. It is a very stable compound, mercuric oxide, iodine, ammoniacal silver solution, and alkaline lead salts, being without action on its alcoholic solution; lead sulphide is separated in the last case, if sodium amalgam is added. It is not decomposed by cold strong sulphuric acid, but dissolves, and is reprecipitated unchanged on addition of water; it gives off sulphurous anhydride when heated with a strong acid. The ethereal solution is not precipitated by hydrochloric acid gas. A nitro-product is obtained by careful treatment with concentrated nitric acid. Heating with metallic potassium gives rise to

the formation of mercaptan and potassium sulphide. Aniline and alcoholic ammonia have no action even at  $250^{\circ}$ , nor has alcoholic potash on short boiling. It forms with bromine a compound which crystallises in needles. By the action of concentrated hydrochloric acid at  $250^{\circ}$ , it splits up into carbonic anhydride, sulphuretted hydrogen, ethylmercaptan, and ethylaniline, which proves its constitution to be that given above. Though it does not combine with ethyl iodide at  $170$ — $190^{\circ}$ , it does so with methyl iodide at  $130$ — $150^{\circ}$ , forming a compound crystallising in fine feathery needles. The hydrochloride of *phenylimidobenzylphenylcarbaminthiethyl*,  $\text{NPh} : \text{C}(\text{NC}_7\text{H}_7\text{Ph})\cdot\text{SEt}$ , is obtained by the action of benzyl chloride on phenylimidobenzylcarbaminthiethyl at  $150^{\circ}$ . This hydrochloride is only sparingly soluble in water, and on boiling with the latter is partially decomposed into acid and base. The free base is solid at the ordinary temperature, together with phenylthiocarbimide. *Phenyldithiurethane*,



is obtained by heating the base,  $\text{NPh} : \text{C}(\text{N.HPh})\cdot\text{SEt}$ , with carbon bisulphide at  $160$ — $200^{\circ}$ .

In connection with this subject compare Wills (*Ber.*, **15**, 338), also Bernthsen and Klinger (*ibid.*, **10**, 492; **12**, 576; *Annalen*, **184**, 192, 197). T. C.

**Action of Amines on Quinones.** By T. ZINCKE (*Ber.*, **15**, 481—484).— $\beta$ -*Naphthaquinone-dianilide*,  $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}$ , can be prepared in several ways. From the  $\beta$ -quinone by mixing and boiling alcoholic solution with excess of aniline, and then boiling for some time; by treating the product with dilute soda the monanilide is dissolved, and the dianilide remains, and is purified by crystallisation from hot alcohol or benzene. The monanilide is easily converted into the dianilide, by simply warming an acetic acid solution with aniline and precipitating with water. It can also be easily prepared from the  $\alpha$ -naphthaquinone, from the hydroxynaphthaquinone, or from hydroxyimido- or diimido-naphthol. From these several methods the author suggests this constitution,  $\alpha\text{OC}_{10}\text{H}_5(\text{NPh})_2\text{NHPh}\beta$ , the oxygen being quinonic. It is sparingly soluble in cold alcohol, more easily in hot alcohol, benzene, and toluene. It crystallises in dark red needles with metallic lustre (m. p.  $179$ — $180^{\circ}$ ). Acetic acid dissolves it with violet colour; the anilide is, however, reprecipitated on the addition of water; with concentrated sulphuric it gives a dark violet colour, and is not reprecipitated by water. The *hydrochloride*,  $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}\cdot\text{HCl}$ , is precipitated from the hydrochloric acid solution of naphthaquinone-dianilide, on the addition of water, in compact golden-green brilliant crystals, soluble in alcohol. It forms compounds with mercury, gold, tin, platinum, and zinc chlorides, which are prepared by mixing the metallic chlorides with the alcoholic solution of the hydrochloride, and then carefully adding water, the compound salts being precipitated. The *platinochloride*  $(\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}\cdot\text{HCl})_2\text{PtCl}_4$ , forms small needles, insoluble in alcohol. The *zincochloride*  $(\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}\cdot\text{HCl})_2\text{ZnCl}_2$ , black-green broad needles, soluble in alcohol with decomposition. The hydrobromide is similar to the hydrochloride. The hydriodide is very

stable, and crystallises from hot alcohol in compact black needles. The *sulphate*,  $C_{22}H_{16}N_2O_7H_2SO_4$ , has a red-brown metallic lustre, can be crystallised from alcohol, and is decomposed by water. The *nitrate* crystallises in black-brown leaflets, scarcely soluble in water, containing nitric acid, soluble in alcohol.

The dinanilide is very stable. It is not attacked by boiling with alkalis, and only very slowly by alcoholic sulphuric acid; among the products of decomposition in this case, hydroxynaphthoquinone (m. p.  $190^\circ$ ) can be recognised. Concentrated nitric acid, nitrous acid, and bromine, yield substitution-products. Reducing agents give rise to colourless compounds which soon become red in the air.

D. A. L.

**Resorcinol Dye-stuffs.** By G. DAMUR and L. SCHREINER (*Ber.*, **15**, 555—557).—Succinic acid or its anhydride, when fused with resorcinol at  $140^\circ$  for several hours, gives a substance which is very similar to fluorescein. This reaction takes place more easily if sulphuric acid or zinc chloride be added to the melt. The product, which appears to be identical with that obtained by Baeyer (*ibid.*, **4**, 664) in a similar manner, and called by him Malins, contains 64.29 per cent. C and 4.35 per cent. H. It is a brown amorphous dye-stuff, which is only sparingly soluble in water, but easily soluble in alcohol. It dissolves in hot concentrated saline solutions, especially of zinc chloride, and separates therefrom on cooling in transparent blood-red crystals, having a metallic lustre. It dissolves in alkalis with a green fluorescence, even stronger than that of fluorescein itself. The neutral sodium salt gives coloured precipitates, the lead compound having the composition  $Pb_2C_{18}H_{18}O_{18}$ . The dye-stuff combines very readily with bromine, forming a substance very similar to eosin; the sodium salt dyes silk and wool like eosin, except that it has a shade of blue.

Succinic acid also forms a similar compound when fused with pyrogallol in the presence of a dehydrating substance. It dissolves in ammonia with a violet, and in caustic soda solution with a blue colour, in these respects, therefore, resembling gallein. Tartaric\* acid also, under similar circumstances, combines with resorcinol, and forms a dye-stuff which fluoresces when dissolved in an alkaline solution. Citric acid,\* glycerol, oxamide, and even dextrin, grape-sugar, and cane-sugar give, with resorcinol, a brownish-red body which dissolves in alkalis with a green or blue fluorescence. Perfectly pure resorcinol, when heated with zinc chloride alone at  $140^\circ$ , gives a body which dissolves in alkalis with an intense green fluorescence and orange-red colour. It seems probable, therefore, that all the products previously described are either mixtures of the dye-stuff obtained by the action of zinc chloride on resorcinol alone, with other dye-stuffs, or consists solely of this dye-stuff. The complete investigation of the latter body is now in hand.

T. C.

**Fluorescein Reactions.** By E. KNECHT (*Ber.*, **15**, 1068—1072).—In a former communication (this vol., p. 728) the author has described cresorcinol, which resembles resorcinol, in giving a fluorescein

\* Compare Frauder, *Ber.*, **14**, 2558.



reaction, the product of which cannot be distinguished from that of resorcinol. Their diacetyl derivatives, however, differ; that of the former melts at  $200^{\circ}$  without change, while that of the latter melts at  $260^{\circ}$  with complete decomposition. From the fact that orcinol,  $[\text{Me} : \text{OH} : \text{OH} = 1 : 3 : 5]$  does not give, while cresorcinol,  $[\text{Me} : \text{OH} : \text{OH} = 1 : 2 : 4]$  gives the phthalein reaction, the author is engaged in examining the hypothesis that the presence of the substituted group in the meta-position to both the hydroxyl groups prevents this reaction, and find in agreement with this view that betorcinol  $[\text{Me} : \text{Me} : \text{OH} : \text{OH} = 1 : 2 : 3 : 5]$  forms no fluorescein.

Among other compounds the author describes a dibromonitrocresol,  $\text{C}_6\text{HBr}_2\text{Me}(\text{NO}_2).\text{OH}$ , crystallising in golden-yellow needles (m. p.  $83^{\circ}$ ), insoluble in water, easily soluble in alcohol and ether, and a metamethylanisidine,  $\text{C}_6\text{H}_3\text{Me}(\text{NH}_2).\text{OMe}$   $[\text{Me} : \text{NH}_2 : \text{OMe} = 1 : 2 : 4]$ , crystallising in silky needles (m. p.  $47^{\circ}$ ), and having an odour similar to that of honey. It is volatile in water-vapour, sparingly soluble in hot water, and soluble in ether.

V. H. V.

**Action of Cyanogen on Picramic Acid.** By P. GRIESS (*Ber.*, 15, 447—453).—When a concentrated alcoholic solution of picramic acid is saturated with cyanogen, and left for about a week until cyanogen produces no more precipitate, *ethoxycarbimidamidodinitrophenol*,  $\text{EtO.CNH.NH.C}_6\text{H}_2(\text{NO}_2)_2.\text{OH}$ , is produced. It crystallises in dark yellow microscopic needles, very slightly soluble in water and alcohol, and insoluble in ether, benzene, and chloroform. It is dissolved easily by cold potash, but is separated from the solution, even by carbonic anhydride. With mineral acids it forms salts, which are decomposed by water into the free acid and base. It is decomposed by boiling with potash or mineral acids. When heated in a test-tube it froths up, changes to a red-brown amorphous substance with evolution of an odour of ethyl cyanide, and on further heating it is completely carbonised. The *hydrochloride*,  $\text{C}_9\text{H}_{10}\text{N}_4\text{O}_6.\text{HCl}$ , forms feebly yellow small rhombic tablets or needles. The above constitution of this body is founded on its analogy to *ethoxycarbimidamidobenzoic acid*. For instance, on boiling this acid with hydrochloric acid it yields *carbamidamidobenzoic acid* and alcohol; this body in the same way yields *carbamidodinitrophenol* and alcohol; and again the acid is changed by ammonia into *benzglycocyamine* and alcohol, and this substance reacts with ammonia in an analogous way, yielding *amidocarbimidamidodinitrophenol*,  $\text{NH}_2\text{CNH.NH.C}_6\text{H}_2(\text{NO}_2)_2.\text{OH}$ , otherwise *dinitrophenolguanidine*, which forms tasteless, scarlet-red, microscopic needles, soluble in water, alcohol, ether, and chloroform. It has the double nature of phenol and base, like the *ethoxycarbimidamidodinitrophenol*; it is, however, a more stable body than this as regards hydrochloric acid, but with potash it is quite as easily decomposed. The *hydrochloride*,  $\text{C}_7\text{H}_7\text{N}_5\text{O}_5.\text{HCl}$ , forms small honey-yellow prisms; it is resolved by water into free acid and base. *Methylamidocarbimidamidodinitrophenol* (*dinitrophenolmethylguanidine*),  $\text{MeNH.CNH.NHC}_6\text{H}_2(\text{NO}_2)_2.\text{OH}$ , is produced by the action of aqueous methylamine on *ethoxycarbimidamidodinitrophenol*; it crys-

tallises in very small yellow needles, and greatly resembles the dinitro-phenolguanidine.

The author discusses the formula of urea, and the respective values of the formulæ  $\text{NH}_2.\text{CNH}.\text{OH}$  and  $\text{NH}_2.\text{CO}.\text{NH}_2$ , and comes to the conclusion that the first formula represents a true urea (a hydroxycarbimide), having the property of combining with both acids and bases and with certain salts, whilst the second represents an unknown body, carbamide; carbamides are indifferent compounds. An example of a true urea is Zinin's monobenzoylurea,  $\text{OH}.\text{CNH}.\text{NHBz}$ , and of a carbamide is Schmidt's dibenzoylcarbamide,  $\text{NHBz}.\text{CO}.\text{NHBz}$ , the product of the action of phosgene on benzamide. D. A. L.

**Oxidation of Pyrogallol in Presence of Gum Arabic.** By P. de CLERMONT and P. CHAUTARD (*Compt. rend.*, **94**, 1254—1256).—When an aqueous solution of pyrogallol is mixed with aqueous solutions of gum arabic of different strengths and exposed to the air, purpurogallin is formed in considerable quantity, as Struve has previously pointed out (*Annalen*, **153**, 160). 10 grams pyrogallol are dissolved in a small quantity of water, mixed with 500 c.c. of a 10 per cent. aqueous solution of gum arabic, and exposed to the air. Purpurogallin is deposited after a few hours, and its formation continues for about two months. At the end of this time 67 parts purpurogallin are obtained for every 100 parts pyrogallol. The gum is removed by repeated decantation with water, the last traces being separated by dissolving the crystals in alcohol. The purpurogallin forms golden-yellow needles, frequently united in bundles, and of the composition  $\text{C}_{20}\text{H}_{16}\text{O}_9$ .

In the formation of the purpurogallin, oxygen is absorbed from the air, but the gum arabic does not act simply as a ferment, for a small quantity of gum will not bring about the oxidation of an unlimited quantity of pyrogallol. The gum itself undergoes some change, but the products of its alteration have not yet been isolated. The gum cannot be replaced by gummic acid. C. H. B.

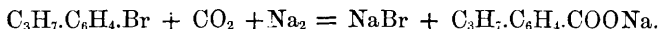
**Tolyl-methyl Ketone.** By A. MICHAELIS (*Ber.*, **15**, 185—186).—Tolyl-methyl ketone is prepared by heating a mixture of acetic anhydride, toluene, and aluminium chloride; it is a liquid of acetophenone-like odour, boils at  $217^\circ$ , and does not solidify on cooling. Dilute nitric acid oxidises it to paratoluic acid; bromine converts it into a crystalline dibromo-compound,  $\text{C}_9\text{H}_6\text{Br}_2\text{O}$  (m. p.  $100^\circ$ ), which can be distilled unchanged. As on heating with potassium acetate the bromine-atoms are replaced, the substitution cannot have occurred in the aromatic nucleus. A. J. G.

**Action of Iodine on Silver Salts of some Aromatic Acids.** By K. BIRNBAUM and H. REINHERZ (*Ber.*, **15**, 456—460).—The action of iodine on silver salts of fatty acids has already been studied (*Abstr.*, 1880, 801). When iodine and silver benzoate are warmed together at  $150^\circ$ , a violent reaction takes place, with evolution of a small quantity of carbonic anhydride. Iodine (2 atoms) is warmed with silver benzoate (1 mol.). As soon as the first action ceases, the

mixture is heated at 160—180° as long as carbonic anhydride is evolved; it is then exhausted with alcohol, filtered from the silver iodide, and after being shaken with mercury to remove excess of iodine, is evaporated and dissolved in sodium carbonate, which leaves an insoluble oily residue: this solidifies after a time, and crystallises from alcohol in almost colourless, transparent, rhombic crystals, containing iodine, melting at 128—130°; and having a diphenyl odour. The sodium salts in solution are converted into barium salts, and the barium benzoate separated from the *metaiodobenzoate* by fractional crystallisation. The latter forms colourless crystals; the free acid melts at 186°. Silver salicylate and iodine also react violently. Equal molecules of them were treated in a similar way to the above. The products are *diiodosalicylic*, *monoiodosalicylic*, and *salicylic acids*, and a small quantity of a resinous body containing iodine. Silver phthalate heated with sufficient iodine to convert the silver into iodide, yields phthalic anhydride, and if the mixture of silver salt and iodine is heated at 170°, a mixture of silver iodide and iodate is left after extracting with alcohol.

D. A. L.

**Constitution of Cumic Acid.** By R. MEYER and E. MÜLLER (*Ber.*, 496—498).—The constitution of cymene is now well understood, and several of its para-derivatives have been synthesised; there is, however, a doubt still surrounding the constitution of cumic acid. The authors make the solution of this question the subject of their experiments; and the way they propose to solve it is to synthesise both cumic acid and the isomeric para-acid by the same method. The theory of the method adopted (Kekulé's reaction) is thus represented:



The cymene employed was obtained by distilling cumic acid with lime; this was brominated by Jacobsen's method. The bromine-derivative, after purification by treatment with alcoholic potash, distillation with steam, and rectification, is mixed with a large excess of benzene,  $1\frac{1}{2}$  times the theoretical quantity of sodium is added, and a current of damp carbonic anhydride passed through for 48 hours, the whole being heated on a water-bath during the operation. From the product a cumic acid is separated, melting at 110°.

D. A. L.

**Azocumic Acid.** By P. ALEXEJEFF (*Jour. Russ. Chem. Soc.*, 1882, 198).—This acid, in the investigation of which the author and I. Kissel are engaged at present, is distinguished from other azo-acids by its easy solubility in alcohol, and by the property of crystallising easily. Its deep red crystals melt at 262°. Its alcoholic solution saturated with hydrochloric acid gave beautiful red crystals of the ethereal salt (m. p. 62°). The sodium salt crystallises from its alcoholic solution in orange-red silky needles.

B. B.

**Phenyl- $\alpha$ -amidopropionic Acid.** By E. ERLÉNMEYER and A. LIPP (*Ber.*, 15, 1006—1007).—Starting from phenylacetaldehyde

the authors have prepared phenyl- $\alpha$ -amidopropionic acid, in order to compare its properties with those of amidohydrocinnamic acid which Posen obtained by the action of ammonia on the addition-product of hydrobromic acid with cinnamic acid. Phenyl- $\alpha$ -amidopropionic acid crystallises in small prisms, which when slowly heated sublime entirely without melting (Posen's compound melts at  $120^\circ$ ). It further differs from Posen's acid in being sparingly soluble in alcohol, readily forming crystalline salts with both acids and bases, and in not giving the smallest trace of ammonium chloride even on repeated evaporation with hydrochloric acid. Hence it appears that Posen's amido- and bromo-propionic acid belong to the  $\beta$ -derivatives. V. H. V.

### Syntheses by Means of Phenylacetylene and its Derivatives.

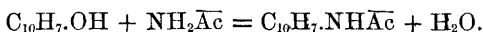
By A. BAEYER and L. LANDSBERG (*Ber.*, **15**, 212—214).—On treating an intimate mixture of the copper compounds of orthonitrophenylacetylene and ethyl acetoacetate with an alkaline solution of potassium ferricyanide, dinitrodiphenyldiacetylene and a new substance,  $C_{19}H_{12}N_2O_3$ , are obtained. The latter crystallises in microscopic yellow needles, is readily soluble in chloroform, and decomposes suddenly at  $165^\circ$  without previous fusion; its constitution may possibly be expressed by  $CH_3.CO.CH(C:C_6H_4.NO_2)_2$ .

By the action of sulphuric acid followed by pyrosulphuric acid on this compound, a dark brownish-red solution is obtained, from which water precipitates red flocks of a substance capable of being crystallised from chloroform, and possessing properties similar to those of the substance belonging to the isatogen-group previously prepared from orthonitrodiphenyldiacetylene.

The authors endeavoured, without success, to prepare ethylnitrophenylacetylene by the action of ethyl iodide on the silver compound of orthonitrophenylacetylene. A. J. G.

### Conversion of Alpha- and Beta-naphthols into Amidonaphthalenes.

By A. CALM (*Ber.*, **15**, 609—616).—Merz and Weith (*ibid.*, **13**, 1298) have shown that when  $\beta$ -naphthol is heated at  $210^\circ$  with the ammonium compound of zinc chloride, it gives dinaphthylamine, together with a small quantity of mono-naphthylamine. The author finds that by using an acid amide, such as acetamide (in practice ammonium acetate, or better a mixture of ammonium acetate and acetic acid) in place of ammonia, the yield of mononaphthylamine is considerably increased, thus:



Under these circumstances  $\beta$ -naphthol (m. p.  $122^\circ$ ) gives chiefly  $\beta$ -acetonaphthalide (m. p.  $132^\circ$ ), together with small quantities of  $\beta$ -dinaphthylamine (m. p.  $170.5^\circ$ , and traces of  $\beta$ -naphthylamine (m. p.  $112^\circ$ ). Under similar conditions  $\alpha$ -naphthol gives  $\alpha$ -acetonaphthalide (m. p.  $160^\circ$ ) in large quantity,  $\alpha$ -dinaphthylamine (m. p.  $111^\circ$ ) in smaller quantity, and only traces of free mononaphthylamine. The nitroso-compound (m. p.  $260^\circ$ ) of dinaphthylamine was prepared and found to be identical with the same compound discovered by

Landschoff (*ibid.*, 11, 638). Tables are given showing the influence of time, temperature, and mass in the above reactions.

If ammonium formate be employed instead of ammonium acetate the formonaphthalide at first formed is at once decomposed into naphthylamine and carbonic anhydride, the yield of both  $\alpha$ - and  $\beta$ -naphthylamine being exceedingly good. T. C.

**Action of Amines on Dichloronaphthaquinone.** By A. PLAGEMANN (*Ber.*, 15, 484—488).—The reaction between the amines and dichloronaphthaquinone can be thus represented:  $C_{10}H_4Cl_2O_2 + NH_2R = C_{10}H_4Cl(NHR)O_2 + HCl$ , only one atom of chlorine being displaced. The action with the primary amines takes place very readily, and the resulting compounds behave generally like the  $\alpha$ -naphthaquinone derivatives. Most of them break up on boiling either with soda or with acids into chlorhydroxynaphthaquinone and the respective amine. The *methylamine* derivative, formed by the action of methylamine on dichloronaphthaquinone, is reddish-yellow (m. p.  $150^\circ$ ); the *ethylamine* derivative is brownish-red (m. p.  $110^\circ$ ), both are soluble in alcohol and soda with a wine-red colour, and crystallise in needles. Aniline acts on the dichloronaphthaquinone, producing *chloronaphthaquinone anilide*,  $C_{10}H_4Cl(NH_2Ph)O_2$ , crystallising in copper-red needles with metallic lustre (m. p.  $207$ — $208^\circ$ ), sparingly soluble in alcohol, easily in hot glacial acetic acid and in alkalis with deep violet colour. A similar compound is produced when chlorhydroxynaphthaquinone and aniline are heated together in a sealed tube for several hours at  $170$ — $180^\circ$ . If an acetic acid solution of chloronaphthaquinoneanilide is warmed with nitric acid or treated with nitrous acid, or potassium nitrite, it is converted into *chloronaphthaquinone-paranitranilide*,



which forms fine blood-red needles (m. p.  $282^\circ$ ), very slightly soluble in alcohol and glacial acetic acid, and giving with alkalis a deep violet colour. The corresponding [1:3] *nitranilide* obtained by the action of [1:3] nitraniline on dichloronaphthaquinone crystallises in yellow-red insoluble needles (m. p.  $245^\circ$ ). The [1:2] anilide has not been obtained. When a slow stream of nitrous gas is passed through the anilide suspended in a small quantity of acetic acid, a nitroso-derivative is formed; it crystallises from benzene in broad yellow needles (m. p.  $126^\circ$ ), soluble in hot soda to a brownish-yellow solution, in which hydrochloric acid produces a blue flocculent precipitate. The nitroso-derivative is converted into the nitro-derivative by both alcohol and acetic acid.

The action of nitric acid (1.4) and of ethyl nitrite, gives rise to a small quantity of a substance crystallising in dark brown fine needles soluble in alcohol, glacial acetic, and benzene, and in soda with a violet colour; with this solution hydrochloric acid forms a red-brown precipitate. Bromine acts on the anilide, producing *chloronaphthaquinone-parabromanilide*, a cherry-red substance melting at  $262^\circ$ , sparingly soluble in alcohol and glacial acetic acid; with soda it yields a deep violet coloured solution. This substance is also produced when dichloronaphthaquinone and [1:4] bromaniline are heated together at  $170$ —

180° in sealed tubes for several hours. Excess of bromine gives rise to two bye-products, one, apparently an hydroxyquinone derivative, crystallising in long yellow needles (m. p. 200°), the other white needles (m. p. 120°). The action of [1:4] toluidine on dichloronaphthaquinone gives rise to *chloronaphthaquinone-paratoluidide*,



which forms crimson prismatic crystals with metallic lustre (m. p. 196°), sparingly soluble in alcohol, easily in glacial acetic acid and in soda with deep violet colour. By the action of potassium nitrite, or nitric acid, or ethyl nitrite, this compound is converted into *chloronaphthaquinonenitro-paratoluidide*,  $\text{C}_{10}\text{H}_4\text{Cl}(\text{NH}.\text{C}_6\text{H}_3\text{Me}.\text{NO}_2)\text{O}_2$ , crystallising in blood-red slender needles (m. p. 236—240°) with silky lustre, sparingly soluble in alcohol and glacial acetic acid, and in soda with violet colour. *Chloronaphthaquinonebromo-paratoluidide* crystallises in mushroom-like groups of cherry-red silky needles (m. p. 185°), sparingly soluble in alcohol, more easily in glacial acetic acid and in soda with the usual violet colour. The [1:2] toluidine derivatives have also been prepared.

*Chloronaphthaquinone-orthotoluidide* forms copper-red crystals with metallic lustre (m. p. 152°). *Chloronaphthaquinonenitro-orthotoluidide* is a blood-red substance (m. p. 230°). *Chloronaphthaquinonebromo-orthotoluidide* is a cherry-red substance (m. p. 212°). Solubilities are somewhat similar to the above, inclusive of the violet coloration. Excess of bromine gives rise in this case also to two bye-products, one, the hydroxyquinone derivative crystallising in yellow needles (m. p. 203°), the other in long white needles (m. p. 50°). Dimethyl- and diethyl-amine act in an analogous way. The *dimethylamine derivative* crystallises in scarlet needles (m. p. 85°), easily soluble in alcohol. The *diethylamine derivative* is resinous and somewhat volatile with steam. Diphenylamine does not form a derivative even in presence of hydrochloric acid; in this respect dichloronaphthaquinone differs from naphthaquinone, which forms a blue compound with diphenylamine.

D. A. L.

**Anthracylamine.** By A. ROEMER (*Ber.*, **15**, 223—226).—An amidoanthracene not having yet been prepared, the author endeavoured to obtain it by reducing nitroanthraquinone with zinc and ammonia; nitrogen, however, was evolved, and a substance crystallising in needles (m. p. 80°), apparently dihydraanthol, obtained. Amidoanthraquinone on treatment with zinc and ammonia, also yielded a substance which was not the desired amido-anthracene. By heating together hydriodic acid (sp. gr. 1.7), amorphous phosphorus, and amidoanthraquinone for  $1\frac{1}{2}$  hours, a reddish-brown crystalline mass is obtained, which on boiling with dilute hydrochloric acid completely dissolves; on cooling, brilliant white plates of *anthracylamine hydrochloride* separate. On treatment with ammonia, *anthracylamine*,  $\text{C}_{14}\text{H}_9.\text{NH}_2$ , is obtained in yellow plates (m. p. 238°); it can be sublimed, and is sparingly soluble in water, the solution having a yellow colour and green fluorescence. When the reduction of the amidoanthraquinone is carried on for a shorter time, another basic substance is found in the

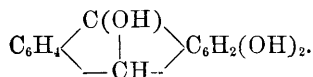
wash-water from the anthracylamine; it is apparently an intermediate product between amidoanthraquinone and anthracylamine.

A. J. G.

**Tetranitro-isoanthraflavic Acid.** By H. ROEMER and M. SCHWARZER (*Ber.*, **15**, 1045—1047).—Isoanthraflavic acid differs from alizarin, not only in its behaviour towards reducing agents, but also in being unattacked by nitric acid under conditions under which  $\beta$ -mononitroalizarin is formed. Cold fuming nitric acid gives with isoanthraflavic acid a tetranitro-derivative,  $C_{11}H_4(NO_2)_4O_4$ , which crystallises in golden glistening leaflets melting at  $300^\circ$ , easily soluble in water, alcohol, and ether, to form red golden solutions. It dissolves in alkalis and ammonia, giving a deep red coloration, converted by boiling with zinc-dust into a dark green, and by sodium hydrosulphide into a deep violet. It dyes silks and wools an orange gold, but has no effect on mordants, and thus differs from mononitroalizarin, which dyes mordants, but not silks and wool. The potassium salt crystallises in silky ruby-red needles, the silver salt in glistening red-brown needles. Anthraflavic acid and anthrarufin resemble isoanthraflavic acid in giving tetranitro-derivatives; but as it has been established that in both the former dioxyanthraquinones one hydroxyl-group is in each benzene nucleus, so this similarity of behaviour lends support to the view that isoanthraflavic acid has a similar constitution.

V. H. V.

**Deoxyanthraflavic Acid.** By H. ROEMER and M. SCHWARZER (*Ber.*, **15**, 1040—1045).—One of the authors has already described (*Abstr.*, 1881, 823) deoxyalizarin, a reduction-product of alizarin, probably represented by the constitutional formula,



In the present communication the authors examine the product of reduction of isoanthraflavic acid (from  $\beta$ -anthraquinonedisulphonic acid) with zinc-dust and ammonia under conditions similar to those used in the reduction of alizarin. An isomer of deoxyalizarin was obtained in golden-yellow glistening needles (m. p.  $330^\circ$ ) insoluble in water and benzene, soluble in alcohol, acetone, and acetic acid. It dissolves in concentrated sulphuric acid and alkalis to form a red solution having a bluish-green fluorescence, giving no absorption-bands (thus differing from deoxyalizarin, which gives a strong absorption-band near D). With acetic anhydride it forms a diacetyl derivative,  $C_{11}H_8Ac_2O_3$ , which crystallises in white glistening needles melting at  $173^\circ$ , soluble in alcohol and forming a colourless solution with blue fluorescence, insoluble in cold dilute alkalis. As anthraflavic acid has been shown to contain one hydroxyl group in each benzene nucleus, it is probable that isoanthraflavic acid, from its formation and similarity in chemical properties, possesses a similar constitution.

Of the two possible constitutional formulæ for deoxyisoanthraflavic

acid, viz.,  $\text{OH} \cdot \text{C}_6\text{H}_3 < \begin{smallmatrix} \text{CO} \\ \text{CH}_2 \end{smallmatrix} > \text{C}_2\text{H}_3\text{OH}$ , or  $\text{OH} \cdot \text{C}_6\text{H}_3 < \begin{smallmatrix} \text{C H} \\ \text{O} \\ \text{C H} \end{smallmatrix} > \text{C}_6\text{H}_3 \cdot \text{OH}$ , the

authors incline to the former, and they farther draw attention to this compound as the first representative of a new class of compounds intermediate between deoxyanthraquinone and deoxyanthracene.

V. H. V.

**Azoanthrol Colours.** By C. LIEBERMANN (*Ber.*, 15, 510—511).—By mixing alkaline solutions of anthrol with solutions of diazo-bases or their sulphonic acids, the author has obtained azoanthrol dyestuffs analogous to the azophenol and azonaphthol colours. The colours containing the sulphonic group are soluble in water and alcohol, whilst the others are insoluble. The tone of the colour lies between blood-red and red-brown. It is evident that several other anthracene derivatives can be used for the preparation of analogous azo-colours.

D. A. I.

**Colouring Matters from Chinese Yellow-berries, Capers, and Rue.** By P. FOERSTER (*Ber.*, 15, 214—217).—*Sophorin*, the glucoside of Chinese yellow-berries (from *Sophora Japonica*) is not identical with quercetin, or apparently with rutin; on treatment with dilute sulphuric acid, it yields isodulcicite (57·5 per cent.) and *sophoretin* (46·8 per cent.), a substance very similar to quercetin, but differing in its derivatives. *Sophorin*, unlike quercetin, cannot be brominated without decomposition; it yields isodulcicite and bromsophoretin.

The glucoside of capers (*Capparis spinosa*) on treatment with dilute acids yields isodulcicite (about 57·5 per cent.) and 47·8 per cent. of a yellow substance requiring further investigation.

The glucoside of rue (*Ruta graveolens*) on similar treatment yields 46 per cent. of quercetin and 55·5 per cent. of a sugar which has not yet been obtained in the crystalline state.

A. J. G.

**Constituents of Podophyllin.** By V. POWISSOTZKY (*Pharm. J. Trans.* [3], 12, 1011—1013).—In a former paper the author attributed the physiological action of podophyllin to two crystalline active principles; he now shows that it is alone due to a neutral crystalline substance, *picropodophyllin*, into which, and an inactive resin-acid, *picropodophyllic acid*, can be converted; he confirms the presence of an inactive resin, and two fatty bodies, as well as decomposition products and inorganic matter.

*Picropodophyllin* (m. p. 200—210°) crystallises in slender colourless silky needles, readily soluble in chloroform and alcohol (90—95 per cent.), more sparingly in weaker spirit, also in ether and glacial acetic acid and picropodophyllic acid; water, turpentine, and light petroleum do not dissolve it. It has an intensely bitter taste and a neutral reaction. Ammonia does not precipitate an alcoholic solution of picropodophyllin, but on evaporating the mixture over a water-bath, it is converted into an amorphous inactive acid; picropodophyllin decomposes when heated to 260° to 278°; alkalis do not readily act on it. When administered internally, it causes vomiting and frequent evacuation, followed by death; in subcutaneous injections it is without effect, since it crystallises where injected.



*Podophyllotoxin* is a very bitter, white, and resinous powder, soluble in dilute alcohol, ether, chloroform, and hot water, and is deposited from the latter in flocks on cooling; it is insoluble in light petroleum. By treatment with calcium or barium hydroxide, podophyllotoxin yields picropodophyllin, since the latter is held in solution by the picropodophyllic acid. Podophyllotoxin has a more rapid action on the system than the difficultly soluble picropodophyllin.

*Picropodophyllic acid* is an inactive resin acid soluble in hot water; cold water precipitates it from its alcoholic solution, and acids from its combinations with alkalis. It can be freed from picropodophyllin only with great difficulty. When podophyllotoxin is heated with calcium or barium hydroxide, the clear solution gelatinises on cooling. On adding an acid to the clear hot solution, flocks are precipitated which under the microscope are seen to consist of jelly-like globules of the acid enclosing crystals of picropodophyllin.

*Podophylloquercetin* crystallises in short yellow needles with a metallic lustre, soluble in alcohol and ether, sparingly in chloroform, insoluble in water. It forms bright yellow solutions with caustic alkalis, and insoluble compounds with the alkaline earths. It is decomposed by continued action of the alkalis, and assumes a green colour on exposure to the air. It melts at  $247-250^{\circ}$  with partial decomposition and partial sublimation. With ferric chloride it gives a dark green coloration, whilst with neutral lead acetate it forms an orange-yellow precipitate soluble in acetic acid. In many respects it resembles other quercetins.

*Podophyllic acid* is insoluble in ether, light petroleum, and water, but soluble in alcohol and chloroform. It is physiologically inactive.

The extraction of the constituents of podophyllin is carried out as follows:—

*Podophyllotoxin*.—The coarsely powdered root is extracted with chloroform free from alcohol. The chloroform is distilled till the extract is reduced to a syrup, when it is slowly poured into two volumes of pure absolute ether. When podophyllotoxin and fatty matters are dissolved, the podophyllic acid separating out in flakes, it is essential that the ether be in excess and free from alcohol, otherwise some of the podophyllic acid remains in solution. The ether-chloroform solution is allowed to drop into twenty times its volume of light petroleum, when podophyllotoxin separates out as a white powder, whilst the fixed oil and fatty matters remain dissolved. The precipitate is dried at  $35^{\circ}$ , dissolved in the smallest possible quantity of chloroform, and the solution filtered with light petroleum, adding a few drops of water to moisten the precipitate as it falls; it is afterwards dried at low temperature. Podophyllotoxin is a white or pale powder, which is not decomposed by light. Podophyllotoxin may be prepared from podophyllin by the same method, but it is difficult to free it from the decomposition-products which podophyllin contains.

*Picropodophyllin*.—Whether this body be prepared from podophyllum resin or from the root, the podophyllotoxin must first be obtained; it is then dissolved in alcohol, mixed with excess of freshly slaked lime and dried over a water-bath; the residue is exhausted by repeated boiling with absolute alcohol, and the solution filtered through

a heated funnel. On cooling, picropodophyllin separates out in long snow-white silky needles.

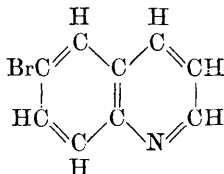
*Picropodophylllic acid* is obtained from podophyllotoxin by treatment with ammonia, but owing to the decomposing action of the alkali, it is difficult to obtain in a state of purity.

*Podophylllic acid* is obtained from the chloroform solution of the crude podophyllotoxin by treatment with ether. It is purified by repeated treatment with chloroform and ether.

*Podophylloquercetin* is best obtained from podophyllin which has been prepared without the use of alum, by exhausting it with chloroform and light petroleum, and after drying with ether, the ethereal solution is evaporated and then treated with lead acetate. The lead compound formed is decomposed in the usual way, and the podophylloquercetin taken up with ether on evaporating the solution; it is obtained as a yellow powder, which gradually turns green on exposure to the air. Sulphuric acid precipitates podophylloquercetin from its ammoniacal solution in minute yellow crystals.

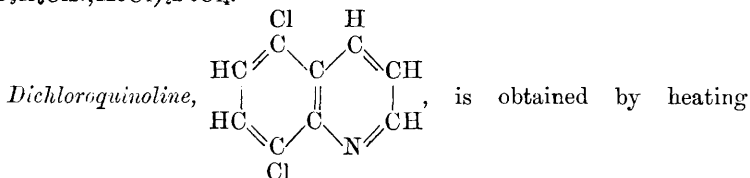
Guareschi's opinion that the active principle of podophyllin is a glucoside is incorrect; neither is it due to berberine, as several authors maintain, since it does not contain that alkaloid. Bucheim's theory that its activity is due to a decomposable anhydride, and that of Power, who attributes it to podophylllic acid, are in error, since the author shows that the physiological action of podophyllin and podophyllum root is solely due to picropodophyllin. L. T. O'S.

**Halogen-derivatives of Quinoline.** By V. LA COSTE (*Ber.*, 15, 557—563).—*Bromoquinoline* may be very readily obtained by heating together a mixture of parabromaniline with the corresponding quantity of glycerol, sulphuric acid, and nitrobenzene; bromoquinoline prepared in this way boils at 276—278° (at 270°, when made direct from quinoline). Its formation from parabromaniline shows that the bromine and nitrogen atoms must be relatively in the positions represented as follows:—



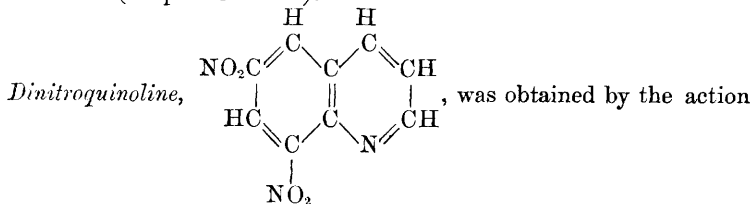
The platinochloride crystallises in small needles having the composition  $(C_9H_6BrN, HCl)_2PtCl_4 + 2H_2O$ . Bromoquinoline, when heated with sodium ethylate in alcoholic solution at 160—170°, does not form ethoxyquinoline, as might be expected, but quinoline itself, together with a considerable quantity of resinous bodies. Dibromoquinoline,  $C_9H_5Br_2N$ , obtained together with the bromoquinoline (probably owing to the presence of some dibromaniline), crystallises from alcohol in slender colourless needles (m. p. 100—101°; dibromoquinoline obtained direct from quinoline melts at 124—126°). The platinochloride has the composition  $(C_9H_5Br_2N, HCl)_2, PtCl_4$ .

*Monochloroquinoline*,  $C_9H_6ClN$ , may be obtained in a similar manner from bromoquinoline, by substituting parachloraniline for the bromaniline. It is a liquid (b. p.  $256^\circ$ ) having a slightly aromatic odour, and is colourless, but very rapidly becomes yellow, and finally brown, on standing for a few hours. The hydrochloride crystallises in colourless needles, which are very soluble in water, and forms a platinochloride  $(C_9H_6ClNHCl)_2PtCl_4 + 2H_2O$ . The bromine and nitrogen atoms in chloroquinoline are in the same position as in the corresponding bromine-derivative. It combines with methyl iodide, even at the ordinary temperature, forming the *methiodide*,  $C_9H_6ClN, MeI$ , which could be obtained only in bright yellow crystalline crusts. It is easily soluble in water, less soluble in alcohol, and still less soluble in ether. The iodine may be readily replaced by chlorine by treating its aqueous solution with freshly precipitated silver chloride; the *methochloride* thus obtained forms an orange-yellow crystalline platinochloride,  $(C_9H_6ClN, MeCl)_2PtCl_4$ .



together a mixture of dichloraniline [ $NH_2 : Cl : Cl = 1 : 2 : 5$ ], glycerol, sulphuric acid, and nitrobenzene. It crystallises from alcohol in concentric groups of short colourless needles (m. p.  $92-93^\circ$ ; volatile without decomposition), and from ether in leaflets. It is easily soluble in alcohol or ether.

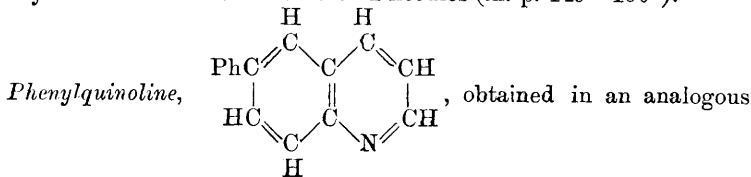
An isomeric *dichloroquinoline* was obtained from the dichloraniline prepared by the action of chlorine on acetanilide. It is less soluble in alcohol than the preceding compound, and crystallises in fine colourless needles (m. p.  $103-104^\circ$ ).



of glycerol, sulphuric acid, and nitrobenzene on dinitroaniline,



It crystallises in fine brilliant brown needles (m. p.  $149-150^\circ$ ).



manner from paramidodiphenyl, crystallises in rosettes of colourless rhombic leaflets (m. p. 108—109°). It is non-volatile in steam, but apparently distils at a higher temperature without decomposition. It forms a non-crystallisable hydrochloride, and an orange-yellow crystalline platinumchloride  $(C_9H_6PhN, HCl)_2PtCl_4$ . T. C.

**Behaviour of the Addition-products of Quinoline and Monohaloid Paraffin-derivatives with Silver Oxide.** By W. LA COSTE (*Ber.*, 15, 186—198).—From experiments on the additive product of benzyl chloride and quinoline, Claus and Himmelman (*Abstr.*, 1881, 182) conclude that this benzylquinone chloride is not of the nature of a quaternary ammonium compound, and therefore that the formula generally accepted for quinoline is incorrect. The author has reinvestigated this question, employing the additive compounds of bromoquinoline and the monohaloid paraffin-derivative, and finds that the substances produced are essentially quaternary ammonium compounds; when treated with silver oxide they yield strongly alkaline solutions, apparently hydroxides, from which the corresponding oxides can be obtained by evaporating the solution.

On adding silver oxide to an aqueous solution of monobromquinolinemethyliodide, a liquid of strongly alkaline reaction is obtained, which, on evaporation, yields monobromoquinolinemethyloxide,



in brilliant colourless needles (m. p. 146—147°), readily soluble in hot alcohol, sparingly in cold alcohol, ether, or water; the aqueous solution does not react alkaline. It is not affected by dilute hydriodic or hydrochloric acid; neither does heating it with concentrated acids convert it into an iodide or chloride, resinous products being formed. As the strongly alkaline solution at first obtained readily yields monobromoquinolinemethyliodide or chloride on treatment with the respective acids, it would appear to contain the hydroxide which, on heating or standing, is decomposed into water and the oxide. All attempts, however, to isolate the hydroxide or the corresponding ethyl compound, were unsuccessful.

On heating dibromoquinoline with methyl iodide at 100° for some time in sealed tubes, they unite to form *dibromoquinolinemethiodide*,  $C_9H_6Br_2NMeI$ , which crystallises in deep red needles, resembling those of alizarine, does not fuse, and cannot be volatilised without decomposition. The corresponding chloride gives with platinic chloride a yellowish-white pulverulent precipitate of  $(C_9H_5NMe)_2PtCl_6$ . By treatment of an aqueous solution of the iodide with caustic soda, dibromquinolinemethoxide is obtained, as a fine powder consisting of minute needles.

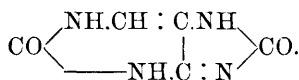
Silver oxide, when acting on aqueous quinolinemethiodide, gives a strongly caustic solution, which, by evaporation in a vacuum, gives a crystalline mass, too impure however for analysis. Quinolinemethiodide (2 mol.) unites with bromine (1 mol.), forming, most probably, a mixture of  $C_9H_7NMeBr$  and  $C_9H_7Me.OBr$ , the aqueous solution giving most of the reactions for hypobromites. *Quinoline methoxide*

was apparently obtained by the action of soda on quinoline methiodide, it forms crystalline crusts that turn red on drying.

Orthoquinoline-benzcarboxylic acid unites with methyl iodide, yielding a compound,  $C_9H_6(CO.OH)NMeI$ . On treating this in aqueous solution with silver oxide, a liquid is obtained free from iodine or silver; this solution, when evaporated on the water-bath, gives orthoquinoline-benzcarboxylic acid, the ease with which the methyl-group, &c., is split off again, speaking for the ordinary quinoline formula.

A. J. G.

**Conversion of Xanthine into Theobromine and Caffeine.** By E. FISCHER (*Ber.*, 15, 453—456).—Xanthine,  $C_5H_4N_4O_2$ , contains 2 atoms of carbon and 4 of hydrogen less than theobromine,  $C_7H_8N_4O_2$ . Strecker (*Annalen*, 118, 172) suggests that the latter is a dimethyl-derivative of the former; he was not, however, successful in his experiments, for by treating silver xanthinate with methyl iodide, he obtained an isomeride of theobromine. The author has repeated the experiment, using the lead- instead of the silver-derivative. Lead xanthinate (dried at  $130^\circ$ ) is heated in a sealed tube at  $100^\circ$  for 12 hours, with  $1\frac{1}{4}$  times its weight of methyl iodide. The product is boiled and extracted with water. The solution is freed from lead by sulphuretted hydrogen, then saturated with ammonia, and concentrated by evaporation. Theobromine crystallises out; its identity was established by converting it into caffeine by Strecker's method. Hence, according to the author's scheme for the graphic representation of caffeine, &c. (this vol., 628), xanthine can be thus represented:—



It will be seen that the first methyl-groups introduced into xanthine, go respectively into the two carbamide-groups. Xanthine is nearly related to guanine and sarcine.

The fact that the animal products xanthine, guanine, and sarcine, are analogous in constitution to the vegetable bases, caffeine and theobromine, tends to show that they are produced in the organism from similar substances by the same chemical process; the author suggests that they are formed synthetically from a urea and an oxidation product of glycerol. He further suggests the preparation of caffeine from guano.

D. A. L.

**Transformation of Morphine into Codeine.** By D. B. DOTT (*Pharm. J. Trans.* [3], 12, 1009).—Grimaux (*Abstr.*, 1881, 829) obtained codeine by the action of methyl iodide on morphine in presence of sodium hydroxide. O. Hesse (*ibid.*, 1553), on repeating Grimaux's experiments, both with sodium and potassium hydroxide, obtained a body which, though closely resembling codeine, differs from it in some important respects, and which he calls  $\beta$ -methyl-morphine.

On repeating Grimaux and Hesse's experiments, the author shows that whether sodium or potassium hydroxide be used, codeine is obtained. The difference of rotatory power between natural codeine

and the synthetic compound is probably due to some impurity. He agrees with Hesse that the generic term "codeine" for the ethers of morphine is objectionable. L. T. O'S.

**Occurrence and Behaviour of Cinchotine, Hydrocinchloridine and Hydroquinidine.** By C. FORST and C. BÖHRINGER (*Ber.*, 15, 519—521).—The authors have discovered that these substances are not oxidation-products, as they previously stated (*Abstr.*, 620 and 830, 1881), but that they exist beforehand in the bark. Oxidised with chromic and sulphuric acids, hydrocinchonidine and hydroquinidine yield respectively cinchoninic (m. p. 253—254°) and quininic (m. p. 280°) acids. D. A. L.

**Piperidine.** By C. SCHOTTEN (*Ber.*, 15, 421—427).—Amylpiperidine, prepared by digesting piperidine, amyl bromide, and potash, is a colourless liquid (b. p. 188°). It combines with methyl iodide with evolution of heat, forming a crystalline mass of *methylamylpiperyl ammonium iodide*, which crystallises from hot alcohol in thick prisms melting at 195°. When distilled with silver oxide it yields, besides a small quantity of amylene, *methylamylpiperidine* (b. p. above 190°); it is a liquid scarcely soluble in water, and lighter than it; its odour is more ammoniacal than that of amylpiperidine. Its *hydrochloride* melts easily, and is hygroscopic. The *platinochloride*,



is slightly soluble in water, melts under water below 100°; in capillary tubes it softens at 100°, and melts at 140°. Methylamylpiperidine can be heated in a sealed tube with hydrochloric acid without being altered, but is decomposed when the dry hydrochloride is heated in a stream of hydrochloric acid gas, and produces a hydrocarbon, methylpiperidine and piperidine. Piperidine is recognised in a mixture of its substitution-products, from the fact that when treated with a dilute acid and potassium nitrite, it forms the nitroso-derivative (see below) which can be extracted by agitation with ether. Methylamylpiperidine combines with methyl iodide, with slight evolution of heat, forming a crystalline addition-product.

*Benzyl-piperidine*, prepared by the action of benzoic chloride on piperidine, is an oil (b. p. 245°) lighter than water, and almost insoluble in it. It combines with methyl iodide, with development of heat, to form the ammonium iodide,  $C_5H_{10}N.C_7H_7.MeI$ , which crystallises from hot absolute alcohol in thick prisms melting at 145°, and decomposing at a higher temperature, giving off benzyl iodide. Treatment with silver oxide converts this ammonium iodide into an ammonium base, which, on heating, is resolved into water, and the volatile *methylbenzyl-piperidine*, which resembles benzyl piperidine in boiling point (245°), and many of its properties. At the same time there are formed small quantities of benzyl alcohol and a low boiling base, probably a compound of methyl-piperidine with methyl iodide. The new base forms a methiodide, which may be crystallised from hot alcohol; it gives off benzyl iodide when heated above its melting point. The ammonium base formed by the action of silver oxide on this iodide,

decomposes at a higher temperature, *piperylene* being among the products of decomposition. Large quantities of methylbenzyl-piperidine and benzyldimethylamine are also formed. There was also a small quantity of benzyl alcohol.

*Nitrosopiperidine* is best prepared by treating a dilute sulphuric or hydrochloric acid solution of piperidine with somewhat more than the calculated quantity of potassium nitrite. Thus prepared it is a yellow aromatic liquid (b. p.  $218^{\circ}$ ), soluble in concentrated hydrochloric acid, from which it is reprecipitated by water; it is heavier than water. When heated in a sealed tube with acids, it is converted into piperidine and nitrous acid; with phosphoric anhydride or zinc chloride a trace of piperylene is formed, but the greater part becomes resinous; treated with sodium amalgam it is reduced to ammonia, piperidine, and a small quantity of a crystalline base which melts at  $58^{\circ}$  and volatilises with steam.

*Piperyluethane*,  $C_5H_{10}N.COOEt$ , the product of the action of ethyl chlorocarbonate on piperidine, is a colourless liquid boiling at  $211^{\circ}$  without decomposition; it has a slightly bitter and astringent taste, a pleasant odour, is heavier than water, almost insoluble therein, and is precipitated by water from its hydrochloric acid solution. It is not at all, or only very slightly poisonous. Boiling with strong potash or hydrochloric acid does not decompose it; when, however, it is heated at  $100^{\circ}$ , in a sealed tube with hydrochloric acid, it is resolved into piperidine, carbonic anhydride, and ethyl chloride. With ammonia or piperidine it yields easily soluble carbamides; it becomes resinous when heated with phosphoric anhydride.

*Acetyl- and Oxalyl-piperidine*.—The former, which is the product of the action of acetic chloride on piperidine, is a liquid boiling at  $224^{\circ}$ , and miscible in all proportions with water. The latter is prepared by heating together equal weights of piperidine and ethyl oxalate, and distilling product. Oxalyl-piperidine,  $(C_5H_{10}N.CO)_2$ , (b. p. above  $360^{\circ}$ ), crystallises in needles melting at  $90^{\circ}$ , soluble in water, alcohol, and ether, insoluble in concentrated alkalis. By heating piperidine with excess of bromine (10 atoms to 1 mol. of piperidine), for four hours in a sealed tube at  $180^{\circ}$ , dibromopyridine is formed.

D. A. L.

**Pirylene.** By A. LADENBURG (*Ber.*, 15, 1024—1025).—From dimethylpiperideine the author has obtained a hydrocarbon, *pirylene*,  $C_5H_6$ , bearing to dimethylpiperideine a relation analogous to that of piperylene to dimethylpiperideine. Dimethylpiperideine combines with methyl iodide with explosive violence to form a hydriodide,  $C_9H_{16}NI$ , which on distillation with soda yields piryene and trimethylamine, thus:



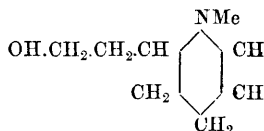
Pirylene (b. p.  $60^{\circ}$ ) is a liquid of peculiar odour, insoluble in water; it does not precipitate ammoniacal copper solution, and is thus distinguished from valylene.

V. H. V.

**Decomposition of Tropine.** By A. LADENBURG (*Ber.*, 15, 1028—1031).—Tropilene yields on oxidation with concentrated nitric acid oxalic and normal adipic acid.

By the action of bromine on tropidine, hydrobromide, ethylene dibromide and dibromomethylpyridine are formed, thus:  $C_8H_{13}N + 4Br_2 = C_2H_4Br_2 + C_6H_5Br_2N + 4HBr$ .

From these reactions some insight may be gained into the constitution of tropine and tropidine; the latter is a hydrogen addition-product, and at the same time an ethylene-derivative of methylpyridine, whose dibromo-derivative is formed in the reaction above. Moreover, from the author's previous experiments (Abstr., 1881, 263), it is probable that the methyl group is directly combined with the nitrogen-atom, so that tropidine may be represented by the formula  $C_5H_6(C_2H_4)NMe$ , and tropine by the formula  $C_5H_7(C_2H_4(OH))NH_2$ . As tropilene on oxidation gives normal adipic acid, the following structural formula for tropine may be considered probable—



V. H. V.

**Tropeine Derivatives.** By A. LADENBURG (*Ber.*, 15, 1025—1027). By the action of nitric acid on tropine, *nitryltropeine* of probable constitution  $C_8H_{11}N(ONO_2)$ , is formed. The hydrochloride of this base may be obtained from the crude product of the reaction by saturating with potassium carbonate, extracting with ether, and then shaking up with dilute hydrochloric acid. With platinum and gold chlorides and with picric acid the solution of the hydrochloride gives crystalline, sparingly soluble precipitates. The free bases could not be obtained in a state sufficiently pure for analysis; but the author infers that the substance contains an  $ONO_2$  group from the fact that potassium nitrate is formed on boiling it with potash.

*Phenylacetropine hydrochloride*,  $C_7H_{11}NO(OC_6H_5)HCl$ , is formed by the slow action of dilute hydrochloric acid on tropine phenylacetate, but the free base could not be obtained in the pure state. The hydrobromide crystallises in dull prisms, the sulphate in tables, the platinochloride in reddish prisms, the aurochloride in glistening leaflets.

*Atrolactyltropine* or *Pseudatropeine*,  $C_8H_{14}NO(C_8H_5O_2)$ , obtained by a method similar to phenylacetropine, is a crystalline substance (m. p.  $121^\circ$ ); it forms a sparingly soluble monochloride and picrate. The mydriatic action of pseudoatropine is analogous to that of atropine.

V. H. V.

**Report on a Memoir on Albuminoïds by A. Béchamp.** By DUMAS and others (*Compt. rend.*, 94, 1276—1281).—The author has isolated different constituents of albuminoïd substances by taking advantage of their different action on polarised light. White of egg contains 50 per cent. of a substance which is precipitated by basic lead acetate, 40 per cent. of a second substance precipitated by ammoniacal lead acetate, and 10 per cent. of a substance which is not coagulated by heat, and is soluble in water, but insoluble in alcohol. These three products are lævogyrate, their rotatory powers being respectively  $34^\circ$ ,  $52^\circ$ , and  $78^\circ$ . The first two possess the general pro-



perties of albuminoids; the third is a ferment, and in all probability plays an important part in the process of incubation. The author was able to split up many other albuminoids, including blood-serum, yolk of egg, milk, wheat-gluten, fibrin, red blood-corpuscles, beef, farina of peas, white mustard, nuts, almonds, &c., into two or more distinct albuminoids and a well defined ferment. The part played by these ferments in the animal economy is a subject for future investigation. The power which fibrin possesses of splitting up hydrogen peroxide into oxygen and water, first observed by Thénard, is peculiar to that portion which, as Bouchardat has shown, is insoluble in hydrochloric acid, and is not possessed by the portion soluble in the acid. This granular insoluble substance has the general properties of albuminoids, and if boiled with water, loses its power of decomposing hydrogen peroxide. It retains this power, however, if dried in a vacuum, also after treatment with alcohol and ether, which remove only a little fat.

All albuminoid substances when oxidised with potassium permanganate yield a certain quantity of urea.

C. H. B.

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## Physiological Chemistry.

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**Digestion of Cellulose.** By W. TAPPEINER (*Ber.*, 15, 999—1002).

—It has been established by Haubner and others that a considerable quantity of the cellulose of the fodder of ruminating animals disappears in the alimentary canal, but researches with the view of isolating a ferment which will dissolve cellulose have hitherto been unsuccessful. The experiments of Hofmeister have shown that this solution is not due to the action of the saliva, and those of Popoff that marsh-gas is evolved in the cloacum, which would seem to arise from the fermentation of cellulose.

In order to investigate this question, the author took weighed portions from the stomach, small intestine, and cæcum of a recently killed ruminant, and divided them into three portions, one of which was allowed to ferment at the temperature of the body; in the second the fermentation was hindered by the addition of antiseptics, which had no influence on the action of unorganised ferments; and in the third the ferments, both organised and unorganised, were destroyed by boiling. In all these cases the quantity of the cellulose was determined. The second and third portions agreed in the quantity of cellulose, but the first portion, in the case of the stomach and cæcum, showed gradually diminishing quantities of cellulose. It would thus appear that the cellulose is dissolved by fermentation in these portions of the alimentary canal. The author also examined the gases evolved by the fermentation of flesh extract, cellulose, and stomach contents; in the case of flesh extract, carbonic anhydride and hydrogen, but in the case of cellulose, marsh-gas and carbonic anhydride were evolved.

Similar results were obtained with paper and cotton, which could be seen by the naked eye to disappear gradually with evolution of marsh-gas.

V. H. V.

**Relation of Asparagine to Animal Nutrition.** By H. WEISKE and others (*Bied. Centr.*, 1882, 312—320).—From researches made by the author, together with Schrodtt and Dangel, it was concluded that asparagine possessed some feeding value, and likewise gelatin, which allowed of a reduction of the albuminoids supplied in food. A more extended series of experiments has been instituted with the view of obtaining further and more exact information on the subject. It was proposed to determine to what extent the portion of the fodder given to sheep would be made use of, when together with an addition of non-nitrogenous food, albumin was also furnished in the one case, asparagine in the other. For this purpose one sheep was fed in the first period with hay, in the second, with hay and bean shudes, and in the third period with hay-starch, and sugar; whilst the second sheep received during the corresponding periods, hay, hay-starch-sugar, asparagine, and hay-starch-sugar and gelatin. The nitrogen given in the gelatin and asparagine corresponded with that in the beans.

The results of the first feeding period showed that the coefficient of digestion for albumin of hay in both sheep was practically the same, viz., 63·47 per cent. and 61·87 per cent. The addition of starch and sugar (sheep 1, period 3) reduced the coefficient to 58·66 per cent.

When gelatin and asparagine were given, a larger amount of nitrogen was digested; but supposing that the whole of these were absorbed, and then subtracting the amount of their nitrogen from that found to be digested, it appears that in reality there is less of the albuminoid nitrogen absorbed; in fact the addition of starch-sugar reduces the digested albumin, but the further addition of asparagine somewhat raises the quantity. The experiments with geese proved that asparagine and gelatin without albumin were incapable of supporting life, and causing an increase in weight, but when they were given together with albumin a saving of the latter was experienced. With ewes it was found that asparagine saved albumin, and aided in the production of milk.

E. W. P.

**Composition of the Milk of Wet-nurses.** By C. KRAUCH (*Arch. Pharm.* [3], 20, 101—104).—It is frequently necessary to bring up a child on cows' or wet-nurses' milk; but if the milk of the latter is abnormal, which is often the case, owing to poor living and hard work, that of cows is preferable. The first analysis represents average human milk according to König, the others are examples of abnormal milk: a child which had been fed with milk of the second nurse, B, suffered severely from abscesses.

	Average human milk.	Wet-nurse A.	Wet-nurse B in 11th month of lactation.	
			Oct. 6.	Oct. 11.
Fat. ....	3.90	6.22	2.25	1.98
Casein, &c. ....	2.48	1.38	0.72	0.75
Lactose ....	6.04	7.29	7.31	7.04
Ash ....	0.49	0.24	0.16	0.18
Water ....	87.09	84.87	89.56	90.05

E. W. P.

**Free Fatty Acids in Cows' Milk.** By C. ARNOLD (*Arch. Pharm.*, [3], 20, 291—293).—The milk of a certain cow was remarkable for its peculiar taste; analysis of the said milk showed an abnormal amount of fat, viz., 4.85 per cent. at sp. gr. 1.029 and 5.45 per cent. at sp. gr. 1.024. Of this quantity about 0.8 per cent. was free acid. Free oleic acid was detected, but the quantity was not estimated; probably free caproic, caprylic, and caproic acids were likewise present.

E. W. P.

**Chemical Theory of the Physiological Action of Arsenic.** By J. DOGIEL (*Ber.*, 15, 572—574).—A reply to criticisms by Binz and Schülz (*Ber.*, 14, 2400) on a paper by the author on the above subject (*Pflüger's Archiv.*, 24).

T. C.

## Chemistry of Vegetable Physiology and Agriculture.

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**To what Extent is Sprouted Grain capable of Further Germination?** By A. E. EHRHARDT (*Bied. Centr.*, 1882, 320—322).—It is well known that the seeds of monocotyledonous plants which have begun to germinate, and then been stopped, will again commence to grow, but the extent to which this first growth must proceed before a second is rendered impossible, is unknown. Rye-seeds were therefore allowed to germinate from periods of time varying from 18—103 hours; at the end of each period they were dried. Allowed to sprout again, 96 per cent. of those which had germinated for only 18 hours were alive, and of those whose first period of growth was 103 hours, only 54 per cent. continued to grow. It seems that about 190 hours is the longest period during which a seed may germinate with any chance of remaining alive after drying. E. W. P.

**Formation of Xanthine Bodies in Germinating Plants.** By P. SALOMON (*Bied. Centr.*, 1882, 356).—The decomposition of albumin in plants resembles the same change in animals, as hereby leucine, tyrosine, glutamine, and aspartic acid are formed. In 100

per cent. of sprouting lupines 0.2 gram xanthine-compounds were found, and these are only found after germination has commenced. These compounds are apparently hypoxanthine and xanthine, no uric acid being detected. For the preparation of such bodies small coombings are recommended as the best source. E. W. P.

**The Time at which Potash exercises the greatest Influence on Plants.** By V. T. MAGERSTEIN (*Bied. Centr.*, 1882, 350—352).—From this preliminary article we gather that plants (potatoes) require potassium most in the earliest stage of their growth, and that later applications of potash manures have but little influence on the increase of reserve matter. Potash should therefore be applied before sowing, and thoroughly mixed with the soil. The depth at which it should be placed is dependent on the length of the roots of the plant. E. W. P.

**Analysis of White Willow (*Salix Alba*).** By A. PETERMANN (*Bied. Centr.*, 1882, 358).—Air-dried, the twigs contained  $H_2O$ , 8.23; organic matter, 89.74; ash, 2.03 per cent. Calculating from the composition of the ash, it is found that a crop of willow (3120 kilo. per hectare) removes from the soil 40 kilo. N, 13  $K_2O$ , 7.5  $Na_2O$ , 16.5  $CaO$ , 4.5  $MgO$ , 8.5  $P_2O_5$ . Although no great quantity of food is removed from the soil, yet manure would materially aid the growth and increase the crop. E. W. P.

**Osmorrhiza Longistylis.** By H. L. GREEN (*Pharm. J. Trans.* [3], 12, 999—1000).—The roots and rhizoma of this plant commonly known as sweet cicely, sweet-root, paregoric root, or sweet anise, have a strong aromatic odour and taste, due to the presence of a light brown yellow volatile oil, denser than water, solidifying at  $38^\circ$  to a crystalline mass resembling oil of anise, which it also resembles in taste, smell, and is probably identical with it. In the fresh root containing 68.5 per cent. of moisture, there is present 0.1 per cent. of oil.

The dried root yields to ether a dark brown oleoresinous substance, which is partially soluble in alcohol (95 per cent.), leaving a dirty brown fatty residue soluble in hot and cold chloroform and carbon bisulphide. It is partly saponified by caustic alkalis, an insoluble fatty acid separating from the alkaline solution when it is treated with an acid. The portion soluble in alcohol consists of two liquids of different densities, the heavier having a bright yellow, the latter a dark brown colour. The heavier liquid is insoluble in chloroform; it mixes with water, but dissolves in it only on boiling, separating again when the solution cools. Alkalis darken the colour of the liquid, but it is restored by acids. On evaporating the aqueous mixture to dryness, the residue exhibits the general characters of a resin. The lighter liquid appears to be a mixture of a fixed oil, a fatty substance, and the essential oil of the root; it has a nauseous bitter taste, and is soluble in carbon bisulphide and chloroform.

Alcohol (95 per cent.) extracts from the residue insoluble in ether a nut-brown substance almost wholly soluble in water, the cloudiness

being probably due to the presence of a small quantity of resin. When boiled with sulphuric acid, it yields a glucose.

From the residue insoluble in alcohol, cold water dissolves albumin and tannin, and a substance which reduces an ammoniacal solution of cupric oxide.

Hot water dissolves from the residue, starch and a substance which is precipitated by gelatin, but gives no reaction with ferric chloride.

On treating the residue with ammonia, a brown solution is obtained, whilst dilute sulphuric acid gives a yellow solution; both these solutions are decolorised by animal charcoal.

The air-dried root yields 6·5 per cent. of ash, of which 50 per cent. is soluble in water. It consists of the carbonates, sulphates, chlorides, and phosphates of potassium, calcium, and magnesium.

L. T. O'S.

**Uruguayan Plants.** By SACC (*Compt. rend.*, **94**, 1256—1258).—The leaves of the caoutchouc tree, *Ficus elastica*, have the composition:—

Caoutchouc .....	0·30
Sugar .....	1·10
Tannin (red) .....	1·00
Fibrin .....	1·80
Wax (blue-green) .....	0·43
Starch .....	5·37
Lignose.....	17·00
Ash .....	0·27
Water .....	72·73
	<hr/>
	100·00

In the forests of Uruguay and Paraguay are several other species of *Ficus* which yield caoutchouc, and the author considers that some of these might be cultivated in the warmer parts of Europe.

The other plants examined were (1) the leaves of the *Laurus camphora*, which weigh about 0·70 gram, and when bruised emit an odour of borneol. (2.) A climbing vetch with blue flowers. It is a good forage plant, and is known locally as *Indigo femelle*, from its resem-

	1.	2.	3.
Gum .....	0·10	0·80	1·91†
Sugar .....	5·50	17·00	—
Fibrin .....	9·80	9·00	2·57
Starch.....	14·34	8·40	0·79
Lignose .....	21·60	23·60	2·05
Ash .....	3·00	6·20	2·00
Water.....	43·46	34·60	90·47
Fat .....	2·20*	0·40	—
Albumin.....	—	—	0·21
	<hr/>	<hr/>	<hr/>
	100·00	100·00	100·00

\* Fat and camphor.

† Dextrin.

blance to the indigo plant. The numbers represent the composition of the entire plant. (3.) A white chickweed (*Alsine media*). The ash of this plant consists essentially of silica, with small quantities of sodium carbonate and ferric phosphate. C. H. B.

**"Göldbleiben" of Hops.** (*Bied. Centr.*, 1882, 332).—This disease in which affected hops, though forming tendrils and leaves, do not produce flower heads, is due to an insect which, according to Nessler, belongs to the family of Phytocoridae. This insect resembles a winged bug of an intense light green colour. The head resembles that of a snail, the body being short, thick, and very soft. The young seem to be hatched in the crevices of the bark on the old stems. Barking and scorching the hop stems prevents the propagation of the disease. E. W. P.

**Distribution of Heat and Rain during the Growth of Sugar-beet.** By H. BRIEM (*Bied. Centr.*, 1882, 289—292).—The two most important periods for the growth of sugar-beet are April-May, and August-September. At eleven observing stations it has been found that 24° is the minimum amount of heat necessary for satisfactory growth during the months April-September, and that this quantity should be distributed in the proportions 23 : 41 : 36.

It is only during the first stage that any great variation from the normal temperature is allowable, and in the last a great variation is always injurious. There is not much variation in the rainfall during the three periods, but although the fall in April-May has been really the lowest, yet this period must be considered as the wettest, for there still remains much moisture in the soil. Finally, the results obtained by observation are in accordance with these practical observations of the cultivators, that the weather in the first period should be wet and moderately warm; in the second, weather moist and very warm; and in the last, dry and warm. E. W. P.

**Cultivation of Potatoes.** By SCHÖNEMANN and others (*Bied. Centr.*, 1882, 328—331).—Out of nine varieties, Schönemann finds that Dabersche is the best potato, as giving a high yield and with a high percentage of starch; but at the same time as it ripens only in October, it is less adapted for distillery purposes, while "Alcohol" ripens in September. On account of the situation of the distilleries, it is frequently necessary to grow potatoes on wet heavy soils; of the sorts adapted for this kind of soil, one cultivator finds Dabersche, Eos, and Champion to be the best. Märcker and Rumpf do not find the winter planting of potatoes to be satisfactory, many being lost. Another cultivator recommends the use of a gauge when setting potatoes; he also finds guano of little value. E. W. P.

**"Canna Edulis Sterilis" as Food.** By E. A. CARRIÈRE (*Bied. Centr.*, 1882, 331).—The tubers of this plant are recommended as food both for man and beast; variety *edulis* contains 90 per cent. water, and 1.88 per cent. sugar; and variety *discolor* 80 per cent. water with 0.48 per cent. sugar. This latter variety contains a starch closely



resembling that of arrowroot. As the stems and leaves are rich in nitrogenous matter, they may be cut up and mixed with clover, oats, &c., and used as fodder for animals; as food, the tubers may be boiled and then baked, or eaten as a salad. The cooking should not be conducted in metal vessels, on account of the presence of some acid not yet investigated.

E. W. P.

**Impoverishment of Soils by Removal of Straw.** By HANAMANN (*Bied. Centr.*, 1882, 292—294).—Removal of straw from land tends to render the soil poor: for not only are potash, lime, phosphoric acid, &c., removed, but also a considerable amount of organic matter, whereby the moisture is too much reduced. Valuable analyses of the soil, as affected by removal of straw, are given, which show a loss of 52,159 kilos. organic matter, 2404 kilos. N, and 476 kilos.  $K_2O$  per hectare (22 cm. deep).

E. W. P.

**Contribution to the Agronomic Estimation of Soils.** By M. FESCA (*Bied. Centr.*, 1882, 294—299).—As the fertility and capabilities of a soil cannot properly be determined in the laboratory, the author has carefully studied those properties of the soil (behaviour towards water, &c.) upon which its agricultural value depends. The process of absorption is dependent on chemical changes induced by the easily soluble zeolites; the phenomena of absorption are to be considered as a special phase of weathering, in which the minerals are not only destroyed, chemically and physically, but also other important compounds are formed. Amongst the factors which influence the amount of absorption in any case, is to be reckoned the quantity of water present, which by its solvent action counteracts the absorption; consequently a heavy rainfall reduces the strength of the solution of plant-food in the soil. The author considers that Knop's is by far the best method for estimating the absorptive coefficient of a soil; the process of filtration in which chalk is added is unsatisfactory, and the absorption of phosphoric acid should be determined as well as that of potash and ammonia. The detailed account of the absorption experiments is given, which shows that a definite ratio exists between the quantity of zeolites (soluble in hydrochloric acid) in the soil and the nitrogen absorbed, also that phosphoric acid is retained in proportions increasing with the lime. Silica reduces the absorption. With soils of high absorptive power, increase of the solutions added is accompanied up to a certain point by increase of absorption, but absolute figures have not as yet been obtained. Estimation of absorption by soils is not appreciably influenced by their perfect dryness.

E. W. P.

**Evolution of Free Nitrogen during Putrefaction.** By B. E. DIETZELL (*Ber.*, 15, 551—555).—In various cases of putrefaction (mixtures of blood, cow's urine, gypsum, dried earth, chalk, &c.) it was found that free nitrogen is evolved in quantities varying in different experiments from 5.04 to 17.07 per cent. of the weight of the putrescible substances. The action is also accompanied by the formation of free nitrous acid, leucine, and primary amines, the production

of which explains the evolution of the free nitrogen. For the leucine under the action of the free nitrous acid forms leucic acid and water, whilst a molecule of nitrogen is set free (Sachse). Nitrogen is also set free by the action of nitrous acid on primary amines (Hofmann, *Annalen*, **75**, 363; Meyer and Forster, *Ber.*, **9**, 536; Meyer, Barbieri, and Forster, *ibid.*, **10**, 130), and even on ammonia (Kern, *Landw. Versuchs.-Stat.*, **24**, 368; Schulze). Primary amines also cause an elimination of nitrogen, in that they expel ammonia from ammonium nitrate and are decomposed by nitrous acid. By preventing this action and the formation of free nitrous acid, the loss of nitrogen during putrefaction may be avoided. For this purpose it is recommended to allow solid nitrogenous manures to putrefy with the addition of a proper quantity of chalk until the evolution of nitrous acid has ceased, before they are mixed with the liquid manures.

T. C.

**Manure from Deep Stalls.** By A. EMMERLING and G. LAGES (*Bied. Centr.*, 1882, 300—302).—The manure made in deep stalls was compared with that made after the ordinary manner. The straw was removed by washing, this was analysed, as the well as washings, and the portions soluble in water.

*Feeding Boxes.*

In 1000 parts.	Straw.	Washings.	Soluble in water.	Total.
Dry matter .....	148·1	60·4	20·3	228·8
Ash .....	6·0	10·7	9·6	26·3
P <sub>2</sub> O <sub>5</sub> .....	0·37	0·91	0·14	1·42
K <sub>2</sub> O .....	0·08	0·90	4·69	5·67
N in organic combination	0·88	0·67	1·90	3·15
N as NH <sub>3</sub> .....	—	—	0·66	0·66
Total N .....	—	—	—	4·11

*Manure Heap.*

In 1000 parts.	Straw.	Washings.	Soluble in water.	Total.
Dry matter .....	115·2	51·9	17·9	185·0
Ash .....	5·8	11·2	8·2	25·2
P <sub>2</sub> O <sub>5</sub> .....	0·42	0·52	0·44	1·38
K <sub>2</sub> O .....	0·13	0·50	4·11	4·74
N in organic combination	0·70	0·99	1·18	2·87
N as NH <sub>3</sub> .....	—	—	0·29	0·29
Total N .....	—	—	—	3·16

E. W. P.

**Manurial Effects of Natural Phosphates.** By M. L. GUILLAUME (*Bied. Centr.*, 1882, 302).—The experimental soil was poor in phosphates, containing only 0·05 per cent.; to this stable manure and natural phosphates were applied. The crops produced, although heavier than those on the unmanured land were however not good enough to pay for the expense of manuring. E. W. P.

**Manuring of Soil with various Phosphates at Nancy.** By L. GRANDEAU (*Bied. Centr.*, 1882, 306—312).—On a soil of low quality various crops were grown for eight years, and nitrogenous, non-nitrogenous, and different forms of phosphates with salts of potash were added. Taking the mean yield of all the crops, it was found that precipitated phosphate is equal to superphosphate; bone-meal is but moderate, and phosphorite is poor in its action. Also those manures which contain only potash and phosphoric acid raise the yield above that of the unmanured plots 11·3 per cent., but the increase rises to 40·1 per cent. when nitrogen is given in addition. Four kinds of English potatoes were sown, and of these Mammoth produced the highest, Golden Tankard the lowest yield. Analyses of the roots showed that the first was very deficient in ash, and that the nutrient ratios were widely different, being for Mammoth, 1 : 11; for Champion, 1 : 5·3; Warden, 1 : 11·9; Gold Tankard, 1 : 12. E. W. P.

**Composition of Water in which Malt had been Steeped.** By M. C. LEEUW (*Bied. Centr.*, 1882, 355).

Organic matter.	Mineral matter.	Total dry matter.	N.	K <sub>2</sub> O.	P <sub>2</sub> O <sub>5</sub> .
5·6	5·2	10·8	0·33	1·93	0·31
CaO.	Na <sub>2</sub> O.	MgO.	SO <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Cl.SiO <sub>2</sub> .
0·12	0·47	0·16	0·07	trace	2·12 in 1000 parts.

Such a water as this is well adapted for manurial purposes.

E. W. P.

**Manuring with Osmose Water.** By H. BRIEM (*Bied. Centr.*, 1882, 305).—A large yield of sugar-beet is obtained by the use of osmose water as a manure, but the quality is considerably lowered. In compost heaps concentrated osmose water aids the decomposition of organic matter. E. W. P.

### Analytical Chemistry.

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**Estimation of Sulphur in Pyrites.** By F. BOECKMANN (*Zeits. Anal. Chem.*, 1882, 90).—0.5 gram of the finely powdered substance is fused in a large platinum basin with 25 grams of a mixture of 6 pts.  $\text{Na}_2\text{CO}_3$ , and 1 pt.  $\text{KClO}_3$ , the fused mass is then dissolved, the solution acidified, and precipitated with barium chloride. O. H.

**Sulphurous Acid in Wine.** By L. LIEBERMANN (*Ber.*, 15, 437—439).—The author states that he sent a note to Rösler, head of the laboratory where Haas works, in which he showed amongst other things, that the presence of sulphurous acid could be efficiently proved in several ways by reduction to hydrogen sulphide with sodium amalgam, or by oxidation to sulphuric acid with nitric acid and with hydriodic acid; moreover, that silver nitrate produced precipitates soluble in nitric acid, in alcoholic solutions (the wine distillate is such) of formic, butyric, and valeric acids, and even gives a turbidity in strong alcoholic solutions of acetic acid. Haas does not notice this communication in his paper (this vol., 773). D. A. L.

**Detection of Sulphurous Acid in Wine and other Liquids.** By L. LIEBERMANN (*Ber.*, 15, 439—441).—About 15 to 20 c.c. of the wine are distilled, the distillate is diluted (this is necessary only when the distillate contains alcohol) and shaken with a few drops of iodic acid and chloroform. The chloroform is coloured violet from liberated iodine if sulphurous acid is present; volatile organic acids and aldehydes do not reduce iodic acid under these circumstances. In this way he is able to recognise sulphurous acid in 2 c.c. of a solution containing 1 part in 500,000. In another method the diluted distillate is treated with hydrochloric acid and barium chloride, and then with nitric acid; turbidity shows the presence of sulphurous acid (oxidised to sulphuric). Reference is made to the reduction to sulphuretted hydrogen with sodium-amalgam and hydrochloric acid. D. A. L.

**Suggestions for a Uniform Method of Estimating Soluble Phosphoric Acid.** By M. MÄRCKER (*Landw. Versuchs.-Stat.*, 27, 276—281).—The paper under notice is the result of an arrangement made at the Congress of Members of Agricultural Experimental Stations, held at Danzig, in the year 1880, when it was requested that Prof. Märcker should carry out a series of experiments on the estimation of phosphoric acid soluble in water, and that Dr. Fleischer, of Bremen, should pursue a similar course of investigation into phosphoric acid soluble in citrates. At the Congress of the same body, held in September, 1881, the former reported the results of his experiments. The author does not go into the question of estimating the soluble acid when dissolved, as chemists have a choice of trustworthy methods; neither does he propose to extract from samples all the soluble acid possible to be obtained from them, as 20 litres of water would not be sufficient; but he limits his inquiry to the time most suitable for leaving 20 grams of superphosphate in contact with 1 litre of water, which was the standard agreed to by the Conference of German Agricultural Chemists, at Magdeburg, the time of digestion being settled at two hours. He found that time had a very great influence on the amount of phosphoric acid dissolved, a very remarkable increase being shown in the cases of high class or so-called double superphosphates, and in the lower grades made from phosphorite. The following six examples show the percentage of acid dissolved during digestion, extending over the different periods specified:—

	2 hours.	12 hours.	24 hours.
1 .....	35.63	36.99	37.43
2 .....	36.49	37.03	37.82
3 .....	22.27	22.64	23.32
4 .....	7.10	7.40	7.55
5 .....	7.42	7.58	7.59
6 .....	7.22	7.59	7.71

With other superphosphates he found that the duration of the digestion had no influence on the results. In the following numbers, 7, 8, 9 are made from phosphorite; 10 to 13 from phosphatic guano; 14 and 15 from coprolite; 16 and 17, bones.

	7.	8.	9.	10.	11.	12.
2 hours....	12.88	18.85	8.64	20.03	19.61	15.51
12 hours....	12.99	18.92	8.64	20.17	19.66	15.51
24 hours....	12.99	18.84	8.65	20.16	19.63	15.59

	13.	14.	15.	16.	17.
2 hours .....	19.57	6.98	6.87	16.20	13.23
12 hours .....	19.48	7.04	6.90	16.19	13.25
24 hours .....	19.52	6.99	6.88	16.20	13.23

And in two other experiments a long digestion *diminished* slightly the solubility of the phosphoric acid.

The author thinks that superphosphates of low grades and those of very high should be digested for 24 hours. A doubt having arisen whether the increase was due to an actual solution of the calcium phosphate, or was caused by the acid solution acting on the ferric and aluminium phosphates, the author believes that the former is the true explanation.

Experiments were then made in order to ascertain the effect of prolonged washing on samples of superphosphate. The apparatus was so arranged that half a litre of water should be gradually dropped on 10 grams of the sample, which was placed on a moistened filter, the washings running into a flask containing 10 c.c. of nitric acid; the arrangements were such that the droppings were spread over 5, 10, 20, and 25 hours.

The results were as follows:—

	Washing for			
	5 hours.	10 hours.	20 hours.	25 hours.
Double superphosphate, a ..	34.15	36.80	37.04	37.48
b ..	34.07	36.88	37.39	37.31
Mejillones superphosphate, a	—	18.53	—	—
b	—	18.62	—	—
Bone superphosphate, a ....	—	10.80	—	—
b ....	—	10.91	—	—

Portions of the same samples were digested in 20 grams on 1 litre of water for different times, with the following results:—

	Hours.				
	2.	12.	24.	36.	48.
Double superphosphate, <i>a</i> ..	35.55	36.99	37.32	38.19	38.11
„ „ „ <i>b</i> ..	35.71	36.99	37.55	38.03	38.34
Mejillones superphosphate, <i>a</i>	18.53	—	18.62	—	—
„ „ „ <i>b</i>	18.53	—	18.66	—	—
Bone superphosphate, <i>a</i> ....	10.73	10.70	11.03	—	—
„ „ „ <i>b</i> ....	10.80	10.93	10.89	—	—

It will be seen that digestion yielded higher results in the shorter periods, but washing dissolved more acid eventually. The author does not recommend the employment of the washing process, as the results depend so much on the time occupied.

The use of greater or smaller quantities of water was the next subject of experiment, a litre of water being used with 10 grams and 20 grams of each of the samples; in the cases of superphosphates, either free from or poor in iron, the increased proportion of water dissolves not unimportant additional quantities of phosphoric acid, but in cases of the double and phosphorite superphosphates the increased quantity of water has no effect on the total acid dissolved. It will be seen that in the case of the larger quantity of water, much less of the acid precipitable by sodium acetate is dissolved; thus, although the extra quantity of water actually dissolves more of the total acid, a contrary process goes on, the iron and aluminium phosphates being rapidly precipitated from the more dilute solution. The author does not consider his experiments decisive, and an inspection of the subjoined table will show that, in every case but the second, a marked increase of acid not precipitated by sodium acetate was caused by using the larger quantity of water.

Quality of the superphosphate.	20 grams of substance treated with 1 litre of water.		
	Precipitated by sodium acetate.	Not precipitated by sodium acetate.	Total.
1. Double superphosphate.....	—	—	37.43
2. Phosphorite superphosphate.....	0.48	18.37	18.85
3. Ditto .....	0.73	7.81	8.54
4. Ditto .....	0.83	6.62	7.45
5. Ditto .....	0.60	6.94	7.54
6. Mejillones superphosphate .....	0.25	19.50	19.75
7. Phospho-guano superphosphate ....	—	15.50	15.50
8. Bone-black superphosphate .....	0.25	15.82	16.07

Quality of the superphosphate.	10 grams of substance treated with 1 litre of water.		
	Precipitated by sodium acetate.	Not precipitated by sodium acetate.	Total.
1. Double superphosphate.....	—	—	37·74
2. Phosphorite superphosphate.....	0·27	18·32	18·59
3. Ditto .....	0·38	8·25	8·63
4. Ditto .....	0·30	7·19	7·49
5. Ditto .....	0·38	7·19	7·57
6. Mejillones superphosphate .....	0·15	20·00	20·15
7. Phospho-guano superphosphate ....	—	16·12	16·12
8. Bone-black superphosphate .....	0·22	16 19	16·41

J. F.

**Argentous Oxide.** By W. PILLITZ (*Zeitschr. Anal. Chem.*, 1882, 27).—The precipitate obtained by adding a solution of antimony trioxide to an alkaline silver solution, after treatment with ammonia to remove argentic oxide, is assumed to consist of argentous oxide,  $\text{Ag}_2\text{O}$ . The author shows that the precipitate invariably contains a large proportion of antimony, and that mercury extracts from it both metallic silver and antimony. argentic oxide remaining behind, and that it is perfectly free from  $\text{Ag}_2\text{O}$ . O. H.

**Separation of Barium from Strontium and Calcium in the form of Chromate.** By I. MESCHTCHERSKY (*Jour. Russ. Chem. Soc.*, 1882, 219—224).—Referring to the papers of Fleischer, Pearson, Kaemerer, and Frerichs, who had proposed the separation of the above metals as chromates, either for qualitative or for quantitative purposes, the author proceeds to investigate the properties of the little known strontium chromate. This salt is formed when a strong solution of strontium chloride or nitrate is mixed with one of potassium chromate as a lemon-yellow precipitate, composed of slender microscopic needles. After drying over sulphuric acid or at  $100^\circ$ , the salt does not contain any water of crystallisation, and does not suffer any change on heating. One part of the salt dissolves in 840 pts. of water at  $16^\circ$ . It dissolves in acetic acid only slightly, and with partial decomposition; it is insoluble in alcohol. In order to ascertain whether the solubility of strontium chromate is altered by the presence of different salts, the author precipitated equivalent or varying quantities of solutions of strontium chloride, nitrate, or acetate, with potassium chromate solution, partly in presence of acetic acid; and represents the results of the experiments in a table. He finds that under equal conditions strontium chromate is more easily precipitated from the nitrate than from the chloride, and from the chloride more easily than from the acetate. In a mixture of  $\text{SrCl}_2 + \text{C}_2\text{H}_4\text{O}_2 + \text{K}_2\text{CrO}_4 + 25\text{H}_2\text{O}$ , which does not form a precipitate, the presence of  $\text{Ca}(\text{NO}_3)_2 +$



$C_2H_4O_2 + K_2CrO_4$ , will produce a precipitate. In presence of acetic acid no precipitate will be formed, if the solution contains for 1 mol. of  $K_2CrO_4$  1 mol. of strontium nitrate or acetate, and 30 mols. of water, or for 1 mol. of strontium chloride, 25 mols. of water.

According to the author's determination, 1 pt. of barium chromate dissolves in 23,000 pts. of hot water. In acetic acid it is more soluble than in water. The author confirms the fact that foreign salts, if present, are carried down with barium chromate. The separation of barium from strontium and calcium by means of potassium chromate cannot be therefore regarded as sharp, although, according to the author, it may be used for qualitative purposes, if the solution is neutral and sufficiently dilute, and if, after addition of acetic acid, it is heated and then left at rest for five hours before filtering. It is not necessary to convert the salts first into acetates.

The editor of the Journal (Menschutkin) remarks that he cannot agree with the alteration of the process for application in qualitative analysis, as proposed by the author.

B. B.

### Use of Chromium Phosphate in Analysis and in the Arts.

By A. CARNOT (*Compt. rend.*, **94**, 1313—1315).—If a boiling feebly acid solution of a chromium salt is mixed with sodium acetate and an excess of alkaline phosphate, the whole of the chromium is precipitated in the form of a green hydrated phosphate. This method is applicable to both the green and violet chlorides and sulphates, and to the acetates, but not to the oxalates. It answers equally well with alkaline chromates if sodium thiosulphate is added with the alkaline phosphate, and the liquid boiled for about an hour. In this case the precipitate is mixed with a little sulphur derived from the thiosulphate. The precipitated phosphate has a green colour, and when dried at  $100^\circ$  has the composition  $CrPO_4 \cdot 3H_2O$ . It may be washed with boiling water, in which it is almost insoluble, or, better, first with a warm solution of ammonium acetate to remove alkaline salts, and then with a solution of ammonium nitrate to remove the organic acid. On ignition the phosphate becomes grey, and has the composition  $CrPO_4$ . To separate chromium from aluminium, the former is first converted into alkaline chromate, and the aluminium precipitated as phosphate (*Abstr.*, 1881, 1081). The filtrate is then mixed with sodium thiosulphate and boiled, more alkaline phosphate being added if necessary. The chromium is thus precipitated as phosphate. This method is rapid, and gives accurate results. It is applicable in presence of chlorides and sulphates, and in this respect has the advantage over other methods.

The precipitated phosphate retains its somewhat beautiful green colour when dried, and may therefore be used as a paint instead of other greens, which contain poisonous metals. It may also be employed in dyeing, since it can readily be precipitated on the fibres of the cloth.

C. H. B.

**Difficultly Combustible Substances.** By W. DEMEL (*Ber.*, **15**, 604—605).—In Kopfer's process for determining carbon and hydrogen (*ibid.*, **9**, 1377), the complete combustion of difficultly combustible substances in ordinary organic analysis is easily effected by covering

the substance when placed in the boat with three or four times its weight of platinum-black. T. C.

**Analysis of Wine.** By J. NESSLER and M. BARTH (*Zeits. Anal. Chem.*, 1882, 43).—1. *Determination of Extractive Matter.*—The various methods of determining extractive matter in wine differ not only in the details of manipulation, but also in principle, some chemists including in the term “extractives” all matters other than water, alcohol, or volatile acids; others, only those substances which are not volatile at 100° or 110° C. Thus in the one case the glycerol would be counted among the extractives, but not in the other.

The authors consider that the glycerol should properly be included among the extractive matters, and they recommend that two separate quantities of wine be evaporated, the one with addition of a measured amount of titrated baryta-water, the other without any addition, the residue obtained in the former case being dried at 110–115° for eight hours, in the latter for four hours at 100° in a current of dry air. The addition of baryta (first recommended by Grete) completely binds the glycerol, the difference between the two sets of determinations being glycerol and volatile acids.

From the results of very numerous analyses, the authors conclude that in pure well fermented wines the proportion of extractives (including glycerol) stands in a certain relation to the total acidity. After subtraction of the latter it never amounts to less than 1 per cent. Strongly alcoholic wines always contain more glycerol than weak wines, the glycerol always amounting to from 7 to 10 per cent. of the quantity of alcohol. The mineral constituents usually are about 10 per cent. of the total extract.

2. *On the Optical Properties of Pure and Sugared Wines.*—Neubauer has shown that whilst pure wine which still contains unfermented sugars turns the plane of polarisation to the left, perfectly fermented wine either does not polarise at all or only a few tenths of degrees of Wild's scale to the right; wines sweetened with so-called potato-sugar contain considerable proportions of dextrorotatory non-fermentable substances. The dextrorotatory substances natural to wine are insoluble in strong alcohol, whilst the impurities in potato-sugar are mostly soluble in the same. Neubauer recommended the evaporation of the wine to be tested to one-fifth of the original bulk, the addition of 90 per cent. alcohol as long as a precipitate is formed, then to filter and to mix the filtrate with ether, all optically active substances being then found in the aqueous fluid separating from the ether.

The authors of the present paper show that it is a matter of considerable importance also to remove the tartaric acid present in the wine, and they add, before precipitating with alcohol, a few drops of a strong potassium acetate solution, thus separating the tartaric acid as acid potassium tartrate.

3. *On the Estimation of Chlorine in Wines.*—It is well known to wine falsifiers that chemists lay much stress on the proportion of mineral matters contained in wine, and therefore they frequently add sodium chloride to artificial or adulterated wines, in order to bring the total

amount of ash up to the normal quantity. Such wines do not readily yield a white ash, and a notable proportion of chlorine volatilises during the incineration. Hence the determination of the chloride has to be effected in the wine itself, and not in the ash. The ordinary method of chlorine titration with potassium monochromate as an indicator not being applicable on account of the solubility of silver chromate in the free acid of the wine, and of the obscurity of the end reaction in wines previously neutralised, and Volhard's method likewise giving unsatisfactory results for the reason last mentioned, the authors find it necessary to operate as follows.

50 c.c. of the decolorised wine are acidulated with nitric acid, an excess of standard silver solution is added, and then standard thiocyanate solution is run in until a drop of the liquid when mixed on a plate with ferric sulphate solution just shows a pink coloration.

The proportion of chlorine present in genuine wines usually lies between 0.002 and 0.0025 per cent., and never exceeds 0.006 per cent.

*Detection of Free Tartaric Acid.*—100 c.c. of wine are evaporated to the consistency of a thin syrup and mixed with alcohol as long as a precipitate appears. After a few hours, all cream of tartar has separated, and to the filtrate  $1\frac{1}{2}$  to 2 c.c. of a 20 per cent. solution of calcium acetate are added. Wines free from free tartaric acid remain clear; those with 0.05 per cent. of free tartaric acid give a strong crust of acid tartrate, and those with 0.01 per cent. a plain reaction.

4. *Determination of Citric Acid.*—Pure wines are free from citric acid, or contain only slight traces, whilst in falsified wines that acid is not unfrequently met with.

100 c.c. of the wine are evaporated to about 7 c.c., and precipitated with 80 per cent. alcohol. The acidity of the filtrate is partly neutralised by the addition of milk of lime, and the filtrate from the resulting precipitate is diluted to the original bulk of the wine taken. About 1 c.c. of a cold-saturated solution of neutral lead acetate is added, and the precipitate (containing phosphoric, sulphuric, tartaric, citric, and part of the malic acid) is collected, decomposed with hydrogen sulphide, and the solution of the free acids rendered alkaline with lime, the calcium phosphate removed by filtration, the filtrate slightly acidified with acetic acid, tartrate of lime separating. From the filtrate calcium citrate separates on prolonged boiling. It is collected and dried at  $100^{\circ}$ , the precipitate corresponding to the formula  $(C_6H_5O_7)_2Ca_3 + 4H_2O$ .  
O. H.

**Analysis of Wine and Must.** By R. ULBRICHT (*Landw. Versuchs.-Stat.*, 27, 257—273; see also Abstr., 1880, 586; 1881, 1182).—The use of potassium ferrocyanide as indicator in the estimation of sugar by Fehling's process having been again strongly recommended by Soxhlet, the author experimented with it, partly to learn the cause of previous failures. He now finds that its use greatly facilitates the operation, but that certain precautions must be taken to ensure good results. The temperature must not be high, the filtration must be quickly performed, the time not exceeding two minutes, and the filtrate being perfectly clear; this is difficult to attain, as the copper precipitate is very fine and passes readily through even a threefold

filter of ordinary paper. The filtrate is then slightly acidified with acetic acid, two drops of the ferrocyanide solution is added, and the reaction observed in a beaker of clear glass over a sheet of white writing paper. The presence of alcohol in the wine or must under examination disturbs the estimation considerably. Working with very dilute solutions of glucose and Fehling, the presence of, say, 12 per cent. of alcohol, when the time occupied by the process is 15 minutes, or 6 per cent. when only 5.10 minutes, causes a fine pulverulent light-coloured precipitate, which settles slowly and passes readily through a threefold filter. The presence of but 1 per cent. of alcohol requires a slight but not important increase in the amount of sugar solution necessary to effect reduction; this is dependent on the concentration both of the sugar and copper solutions, and the duration of the warming process; with a Fehling solution of full strength warmed for five minutes it is remarkable, and with one of one-fifteenth the reducing power of the glucose solution warmed for 15 minutes is so much altered that results are quite untrustworthy. The author suggests that these differences are caused by the evaporation of the alcohol causing rapid motion in the liquid, bringing the particles of copper oxide to the surface and on the sides of the beaker, where, meeting the oxygen of the air and being acted on by the alkaline and organic salts contained in the liquid, the copper is oxidised to cupric tartrate and passes into solution; the percentage of alcohol and the duration of the warming process must, therefore, materially affect the results. In cases where great exactness is required, the author recommends duplicate experiments with solutions containing like proportions of sugar and of alcohol.

Chemists differ considerably in their opinions as to the temperature at which the experiment is to be made and its duration. Fresenius (*Quant. Anal.*, 5th Ed.) recommends for volumetric estimations gentle boiling for an unspecified time; for the gravimetric estimation he directs 10 minutes' boiling on the water-bath. Soxhlet, on the other hand, gives definite lengths of time for each sort of sugar. Allihn operates at boiling temperature, but allows the mixture only to commence boiling, and filters at the moment of ebullition; according to the latter, invert sugar and *lævulose* require a longer time than dextrose to reduce the same quantity of copper, owing, probably, to the formation of other reducing compounds during continued heating of the solution. The author previously found that in practice the most trustworthy results were attained by heating the mixed solutions for 15 minutes at 75°, but the presence of alcohol necessitates modification, and he now recommends heating to 85° for five minutes. General instructions are given for the proper carrying out of the process: the reduction is preferably carried out in glass beakers of such capacity that the mixed solutions fill them to within 1 cm. of the edge, the thermometer, which serves as a stirrer, should be attached to a carrier with fine platinum wire, in such a manner that it might touch the bottom but not the sides of the beaker, so that the evaporation of the alcohol should not carry up any fluid between the thermometer and the beaker, so increasing the surface and the danger of undue oxidation.

The reduction in five minutes at 85° is carried out thus. The

Fehling solution is brought to 90—95° C. with frequent stirring with the thermometer, the sugar solution is then added with constant agitation while the temperature is about 90°; the lamp is then removed, the mixture strongly agitated, and five minutes after the 90° is reached it will be about 85°. The mixture is then quickly transferred, with the aid of the thermometer, to a threefold filter (of Duren paper 597) and 40 per cent. of it filtered into a clear beaker, the filter should be kept full, and the filtration finished in one minute; the hot filtrate apparently free from copper oxide is quickly acidified with dilute acetic acid (1 vol. acid to 1 vol. water) and tested with one drop of concentrated ferrocyanide, the beaker being held over a sheet of white writing paper.

Later experiments, not detailed but promised, have convinced the author that the quantity of tartaric or malic acid contained in a wine or grape juice has a remarkable effect on the sugar estimation; the presence of soluble neutral malates in particular delays the process of reduction, and changes the properties of the copper precipitate so that it passes through a threefold filter.

The presence of sulphurous acid, in the proportions usually found in wine or must, exercises no influence on sugar estimation by means of Fehling's solution.

J. F.

**Cause of Jorissen's Reaction for Fusel-oil.** By K. FOERSTER (*Ber.*, 15, 230—232).—Jorissen had proposed to make use of the property possessed by commercial fusel-oil of giving a red coloration with aniline and hydrochloric acid, as a method of testing spirits for the presence of fusel-oil. The author shows that this reaction is due to the presence of furfuraldehyde, and he considers that Jorissen's method is so far not trustworthy in that the appearances described by him are due not to amyl alcohol or its homologues, but to furfuraldehyde occurring as an impurity in the fusel-oil.

A. J. G.

NOTE.—In a later communication (*Ber.*, 15, 574), Jorissen explains that he had never attributed the cause of the coloration to amyl alcohol, the test having been given as one for the detection of fusel-oil in wine; and as Foerster has shown in his paper that furfuraldehyde cannot be separated from fusel-oil by distillation, the test holds good for its intended purpose.

**Examination of Methylated Spirit.** By P. CAZENEUVE (*J. Pharm.* [5], 5, 494—498).—It has been necessary to modify the method for the estimation of methyl alcohol in ethyl alcohol described by Cazeneuve and Cotton (*Abstr.*, 1881, 197), owing to the instant reduction of potassium permanganate by the impure spirit (*mauvais gout de tête*) which contain aldehyde.

The modification consists in distilling 100 c.c. of the alcohol and testing each 10 c.c. of the distillate with 1 c.c. of potassium permanganate solution (5 in 1000). In the case of the alcohol containing wood spirit, each portion of the distillate instantly reduces the permanganate; whereas, if it contain *mauvais gout de tête*, the first 20 c.c. reduce the permanganate at once, whilst the following portions

require an appreciable time. This is readily accounted for, since the aldehyde (b. p. 21°) distils with the first fractions, whilst the acetone (b. p. 38°) present in the wood spirit, to which the reducing action is due, is found in all the distillates.

The results obtained by this method may be confirmed by the iodoform method.

Tables are given showing the delicacy of the method.

L. T. O'S.

### **Estimation of Salicylic Acid in Butter, Milk, and Urine.**

By H. PELLET (*Bied. Centr.*, 1882, 342).—The principles of the method are, extraction, isolation by shaking up the extract with ether, and estimation of the acid present by colorimetric means. For the quantitative method, 200 c.c. milk with 200 c.c. water are heated to 60°, and then 1 c.c. acetic acid is to be added, and an excess of mercuric oxide. After cooling and filtering, the whey is to be agitated twice with 100 c.c. ether, which, after washing, is passed through a dry filter. The residue, after evaporation of the ether, is dissolved in a mixture of alcohol and water, and then titrated with soda solution. In another process 20 c.c. milk are mixed in a mortar with 5 grams precipitated silica, and the mass is then shaken up with 60 c.c. benzene in a narrow tube. After filtration, 20 c.c. are mixed with 10 c.c. water and two drops dilute sulphuric chloride, and the resulting colour is compared with that produced in solutions of known strength.

E. W. P.

**Detection of Foreign Fats in Butter.** By T. TAYLOR (*Bied. Centr.*, 1882, 345).—With a magnifying power of 75, adulteration of butter with suet or lard can be detected, the crystals of the latter being larger than those of the former; use of polarised light and a selenite plate aids the detection of the suet. The presence of vegetable fats may be detected by the addition of two degrees of sulphuric acid to a small quantity of the butter. Under these circumstances pure butter appears as a whitish-yellow opaque liquid, which after five minutes becomes scarlet at the edges. Oleomargarine from suet is at first a transparent amber-coloured liquid, which after 20 minutes becomes of a deep carmine colour. Old or rancid oleomargarine forms a transparent amber liquid, becoming dark brown and opaque in 20 minutes. Fresh oleomargarine from cocoa-nut oil is an opaque pale amber liquid, changing in 20 minutes to a pale red, tinged with violet.

E. W. P.

**Extraction of Alkaloids by means of Oxalic Acid.** By P. E. ALESSANDRIA (*Pharm. J. Trans.* [3], 12, 993—995).—This method consists in digesting a weighed quantity of the bark or seeds with a 2 to 3 per cent. solution of oxalic acid, for from 12 to 24 hours, when the alkaloid is dissolved. To this solution barium hydrate or ammonia is added, when the base is set free, in some cases being precipitated. The precipitate or the solution is extracted with chloroform, ether, or alcohol, according to the nature of the alkaloid. The extract, on evaporation, then leaves the alkaloid in a state of almost absolute purity. The author has applied this method to the extraction of many of the alkaloids with success.

From the bark of *Croton Cascarilla* the author has obtained cascarilline, which he finds identical in its properties with that described by Duval in 1847. In this case the oxalic acid extract is saturated with ammonia, evaporated to two-thirds of its bulk, and any deposit which may form removed by filtration, the solution being then extracted with ether. On evaporating the ethereal solution almost pure cascarilline is obtained. It is soluble in warm water, very soluble in ether and alcohol, sparingly soluble in benzene, chloroform, and carbon bisulphide.

Besides the reactions described by Duval, the author finds that the alkaloid is not decomposed by nitric acid, and forms crystalline salts; it has a bitter taste, and is not precipitated by tannic acid. Cascarilline hydrochloride gives precipitates with tannic acid and phosphomolybdic acid, also a turbidity with iodine. When heated slowly it melts, emitting an aromatic odour; heated with potash, it gives off ammonia.

*Veratrine* is obtained pure and crystalline on evaporating the alcoholic extract of the precipitate obtained by adding ammonia to the oxalic acid solution. In the cases of morphine and quinine the author has extended the method so as to afford a ready means of assaying opium and cinchona barks.

*Morphine*.—The powdered opium is exhausted with 3 per cent. oxalic acid solution. The solution is divided into two equal portions, neutralised in barium hydroxide, and the precipitates collected and washed with water containing alcohol, and dried. One of the precipitates is shaken with alcohol, 90°, and the other with ether or chloroform. The ethereal solution, on evaporation, leaves narcotine, whilst a mixture of the other alkaloids is left by the alcoholic solution.

*Quinine and Cinchonine*.—5 to 10 grams of the powdered bark are made to a thin paste with 3 per cent. oxalic acid solution, shaken with an additional 10 c.c. of the acid solution, and left for 12 hours. The extract is poured off, and the residue washed with water, containing oxalic acid. The solution is divided into two portions, and precipitated with ammonia or barium hydroxide (the latter is preferable, since it precipitates cinchona red). After standing, the supernatant liquid is poured off, and one precipitate is exhausted with ether, which dissolves the quinine, the other with chloroform, in which both alkaloids are soluble. After evaporating the extracts to dryness, the residues are weighed.

*Calumbine* is extracted by the oxalic method from the root of the *Menispermum palmatum*. The oxalic acid extract gives no precipitate with ammonia, but the alkaloid is extracted from the neutralised solution by ether, which, on evaporation, leaves pure white calumbine. This root contains berberine and calumbic acid, in addition to calumbine. The calumbic acid may be isolated by adding acetic acid to the ammoniacal solution after exhaustion with ether.

To extract the berberine, the cold oxalic acid solution is precipitated with barium hydroxide, and the filtered solution heated and allowed to stand 24 hours, when barium oxalate separates out, and carbonic anhydride is passed through the solution, which is filtered, neutralised with ammonia, heated, and twice exhausted with ether, by which

the calumbine is extracted. The remaining solution is evaporated to dryness at 90°, and the residue dissolved in alcohol, from which the berberine is obtained in straw-coloured crystals.

Calumbic acid is obtained from the barium precipitate by treating it with hydrochloric acid, when the acid remains as a dense yellow flocculent precipitate, which is soluble in alcohol. L. T. O'S.

**Influence of Morphine on the Formation of Herapathite.** By E. B. STUART (*Pharm. J. Trans.* [3], 12, 1016).—Iodosulphate of quinine is readily formed in presence of morphine, even though the proportion be 1 to 1000 of morphine. The test is equally delicate with the chlorine test, and may be readily applied as follows:—The salt is dissolved in dilute alcohol by the aid of sulphuric acid, and warmed to 100°. A very dilute sodium solution is then added drop by drop with constant agitation. When sufficient sodium solution has been added, the precipitate suddenly appears and quickly settles. In a mixture of the four principal cinchona alkaloïds, precipitates are formed in the following order; 1st, quinine; 2nd, cinchonidine; 3rd, quinidine; 4th, cinchonine; the last only in concentrated solutions. This method gives good results in all cases, except for the separation of quinine and cinchonidine. On recrystallising from alcohol the two salts may be distinguished by the microscope. L. T. O'S.

**Determination of Nicotine in Tobacco.** By R. KISSLING (*Zeits. Anal. Chem.*, 21, 64).—The author fully discusses the various plans which have been proposed for the above determination, and gives the following as the most trustworthy method:—20 grams of the powdered and dried tobacco are moistened with 10 c.c. of an alcoholic soda-solution, containing 6 per cent. of alkali, and the damp powder is treated for two or three hours in a suitable extractor with ether. From the ethereal solution the ether is then almost completely removed by distillation, and the residue is rendered alkaline by the addition of 50 c.c. of 4 per cent. soda-solution. The nicotine is then driven off in a rapid current of steam, and determined in every 100 c.c. of the distillate by titration with standard acid, rosolic acid being used as an indicator. The author shows that the amount of nicotine in tobacco fluctuates between wide limits. O. H.

**Action of Alcohol and Ether on Tobacco, and the Distillation of the Extract thus obtained.** By J. SKALWEIT (*Arch. Pharm.* [3], 20, 113—119).—The general method for the extraction of nicotine has been already described (*Arch. Pharm.*, 219, 36), and a modification of the process is here recommended, in which during the whole of the operation a stream of hydrogen is passed through the apparatus. A sketch of the apparatus is given. It is found that when the tobacco is treated with 10 c.c. normal sulphuric acid and 200 c.c. of 98 per cent. alcohol, the solution being boiled for two hours with upright condenser, then made up to 250 c.c., and distilled with 100 c.c. potash solution (1·159), all the nicotine is obtained. If potash and ether only are used, a portion of nicotine is left behind.

E. W. P.



**Separation of Ptomaines from Plant Alkaloids.** By H. BECKURTS (*Arch. Pharm.* [3], 20, 104—106).—(Comp. this vol., 430.) In this preliminary notice the author states that he has not yet been able to discover any general reagent which can distinguish between the two classes of poisons. A general reaction for the detection of alkaloids is as follows:—0.01 gram of the alkaloid is dissolved in 5 c.c. acidulated water, and to it are added two drops of 10 per cent. potassium ferricyanide solution, and a drop of very dilute neutral ferric chloride; morphine and colchicine reduce this solution directly, the solution becoming dark blue; less powerful is the reaction—the colour being at first green-blue, precipitation occurring later—exerted by aconitine, brucine, conicine, digitaline, nicotine, strychnine, papaverine, narceine, codeine, and veratrine; picrotoxin (neutral) and atropine give no results. If, then, the ptomaines are reducing substances, this reaction is useless. E. W. P.

**Ptomaines, and their Importance in Judicial Cases.** By T. HUSEMANN (*Arch. Pharm.* [3], 20, 270—289).—The researches of various chemists on the poisonous material found in corpses, in partially decomposed meat, &c., are here detailed and reviewed. A comparison is drawn between the reactions (chemical and physiological) obtained by the Zuetzer-Sonnenschein alkaloid, and that of Selmi and others with atropine and conicine, from which it appears that the substances, although closely resembling one another, are not identical, neither are the alkaloids obtained in the different researches the same.

E. W. P.

**Estimation of Amides in Vegetable Extracts.** By E. SCHULZE (*Zeits. Anal. Chem.*, 1882, 1).—A. Morgen (*Zeits. Anal. Chem.*, 1881, 37) had been unable to obtain satisfactory results by Sachsse's (hypobromite) method. The author explains that Morgen did not keep to the details in working the process laid down by Sachsse, and shows, upon the basis of numerous test experiments, that the method, when properly executed, yields perfectly satisfactory results.

O. H.

**Detection of Magenta, Archil, and Persio in Wines.** By B. HAAS (*Bied. Centr.*, 1882, 337—339).—In applying the process for the detection of magenta (this Journal, 1877 [2], 936) to the detection of archil and persio, the lead precipitate is coloured blue by the first, and violet by the second. The filtrate, shaken up with amyl alcohol, is red in both cases. This reaction is important as serving to discriminate the other two colouring matters from magenta; a further definite test is obtained by treating the amyl alcohol solution with hydrochloric acid and ammonia. Both these reagents destroy the magenta colour, whereas the colour of the other two is not destroyed by hydrochloric acid, and is converted into a violet by ammonia. Ether coloured by magenta is decolorised by ammonia, but not so if archil or persio is present. When König's method is employed (*Ber.*, 1881, 2263), the shaking should not be too violent, or else an emulsion will be formed. In this method also, when archil is present, long-continued heating with ammonia causes the wine to become colourless, but the colour returns on cooling and gentle agitation. The

wort also regains its colour in the air; if the precipitate be rapidly taken out of the hot liquid and well washed, but little colour is retained. These additions to the process render the detection of archil possible. The baryta and magnesia process is useless, as the archil colouring-matter is not precipitated, but the colour is changed to a purple.

E. W. P.

**Analysis of Mustard.** By A. R. LEEDS and E. EVERHART (*Pharm. J. Trans.* [3], 12, 998—999).—The moisture and ash are determined as usual. The mustard oil is extracted with ether as follows:—A weighed portion of the mustard, dried at  $105^{\circ}$ , is placed on a plaited filter-paper, which is introduced into a funnel, with straight ribs, connected with a small tared flask containing ether, by means of a well-fitting cork. To the mouth of the funnel an inverted condenser is attached. The ether is boiled cautiously, whilst its vapour being constantly condensed, falls back on the mustard, extracting the oil. When all the oil is extracted, the ether is distilled off, and the residue dried at  $100^{\circ}$  and weighed. The operation is then repeated with a mixture of equal volumes of alcohol and water, which dissolves the sinapine thiocyanate and potassium myronate. The solution is evaporated, the residue dried at  $105^{\circ}$ , and weighed; it is then ignited and reweighed. The difference gives the weight of sinapine thiocyanate and potassium myronate. By deducting the weight of the latter, the weight of the sinapine thiocyanate is obtained. The residue in the funnel, consisting of myrosin and cellulose, is treated twice with a 0.5 per cent. soda solution, when all the myrosin is dissolved. The residue is washed, dried, and weighed, ignited, and the ash weighed. The difference gives the weight of cellulose.

The soda solution is neutralised with dilute hydrochloric acid, and about 50 c.c. of Ritthausen's copper sulphate solution are added; the solution *exactly* neutralised with dilute soda, and the green precipitate of copper and myrosin collected on a weighed filter, dried at  $110^{\circ}$ , and weighed. It is then ignited and the ash weighed; the difference gives the total amount of myrosin.

This method is preferable to Hassall's, in which the potassium myronate is first determined by converting it into allyl thiocarbamide, and then the total nitrogen and sulphur. After deducting the amount of nitrogen and sulphur required by the potassium myronate, the residual sulphur, and as much of the nitrogen as is required, are calculated as sinapine thiocyanate and the remaining nitrogen as myrosin; but as myrosin also contains sulphur, further calculations are necessary; such calculations are liable to error. However, the results quoted of analyses of brown mustard farina obtained by the two methods are identical.

The authors' method is applicable to cases in which the mustard has been adulterated with starch or flour, since they have determined the complete insolubility of starch in dilute alcohol.

L. T. O'S.

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## Technical Chemistry.

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**Heliographic Engraving in Lines and Half-tones.** By J. M. EDER (*Dingl. polyt. J.*, **244**, 154—157).—Of the two principal methods of heliographic or photographic engraving, viz., the method by means of electrotype and that of etching, the latter has been developed recently to a considerable extent. Talbot's method of preparing heliographic steel engravings forms the starting point (*ibid.*, **128**, 296). Garnier, who has studied this subject during the last fifty years, has published a method which is said to supersede all processes hitherto known. In working the method, it is important to make a distinction between the preparation of linear drawings and of pictures in half-tones.

1. *Heliographic Engraving in Lines.*—A copper plate is covered with a very thin layer of a mixture of 2 grams sugar, 1 gram ammonium dichromate, and 14 grams water, and dried by rotating it over a hot plate. This layer is then exposed under a positive for one minute to sunlight (or three minutes to the electric light). The parts acted on by the light are no longer hygroscopic, whilst the protected parts retain their glutinous consistency, so that dust sprinkled over this part adheres firmly to the mass. In order to render the exposed parts more permanent, it is best to heat the plate strongly. The parts not acted on by the light are porous, and allow a solution of ferric chloride of 45° B. to penetrate, so that etching ensues in the course of a few minutes. Finally, the reserve is removed by washing with ley.

2. *Heliographic Engraving in Half-tones.*—For portraits, landscapes, &c., half-tones are produced by repeating the above operation three times. The prepared plate is exposed under the positive for, e.g., four minutes; only the perfectly black places are copied; they are developed by "dusting" and etching the plate. The latter is then cleaned thoroughly, again treated with the sensitive mixture and exposed under the same picture, placed in exactly the same position for two minutes. On etching, the darker blacks and the less apparent effects come out, and when this operation is repeated a third time with an exposure of one minute, the lightest shades are produced.

3. *Heliographic Engraving for Printing Books, &c.*—To enlarge a linear drawing in relief for printing, the plate is dusted with asphalt and gently warmed. On washing the plate with water, the chromatised sugar is removed, and the asphaltic lines alone remain. Etching with ferric chloride follows this operation; the picture then appears as relief.

4. *Atmography.*—By taking a graved copper plate, filling the hollows with powdered albumin and exposing the plate for a short time to the vapour of hydrofluoric acid, the latter condenses in the powder without attacking the metallic surface. A solution of sugar and borax is then spread over a small surface of metal, paper, or glass, and the two surfaces are brought into contact with one another for a few seconds. By the action of the acid vapour, deliquescent sodium boro-

fluoride is formed; the sugar assumes a glutinous consistency, and on placing a powdered substance on this surface, the picture appears.

Strowbinsky and Gobert propose another method of heliographic engraving. Copper plates are coated with a solution of 5 parts gum, 2 parts ammonium dichromate, and 100 parts water. After drying, the plate is exposed to the light and treated with a solution of asphalt in benzene. The plate is then dried, developed with water, and etched by means of a solution of 30 to 50 per cent. ferric chloride. The asphalt used for strengthening the lines retards the development of the picture. This may be overcome by using albumin. A mixture of 100 c.c. albumin, 50 c.c. water, and 2.5 grams ammonium dichromate is used. The picture is developed with water, dried, and etched.

Mariot has studied the preparation of heliographic engraving on copper and zinc by means of chromatised gum. He dissolves in 630 grams water, 63 grams gum arabic, 21 grams potassium dichromate, 9 grams-grape sugar, and a quantity of ammonia sufficient to give the mixture a straw-yellow colour; 7 grams chromic acid are then added. The etching is done by means of a solution of ferric chloride, dissolved in 4 parts water at 22.5–25°. Under normal conditions, the strong lines appear in half a minute, and the delicate lines in four minutes. After washing with water, the layer is removed with a solution of 5 parts potash in 100 parts water and 100 parts alcohol.

D. B.

**Heliographic Printing.** By J. KAVCIC (*Chem. Centr.*, 1882, 268).

—The original to be copied must be prepared on tracing paper, or rendered transparent by artificial means. A mixture of iron citrate and potassium ferricyanide is painted on paper and dried. The original is then put into the printing frame with its picture side up, and on this the prepared paper is laid. It is now exposed to sunshine in the summer for five minutes, and in the winter for eight minutes. If the sun does not shine, the picture requires one to four hours' exposure, depending on the degree of light. The copy is of a dirty-blue colour, with greenish-yellow lines. As soon as it is taken out of the frame, it is washed repeatedly with water, and finally dried. To produce brown prints, a mixture of uranium and iron nitrate is used; for blacks, silver salts are employed.

D. B.

**Ferro-oxalate-citrate Developer.** By W. DE W. ABNEY (*Chem. Centr.*, 1882, 268).—20 grams potassium citrate are dissolved in 100 c.c. hot water, and the solution is treated with 5 grams iron oxalate, agitated, and filtered. It has a reddish-brown colour, which subsequently changes to greenish-brown. Its action is most powerful in the first state. This developer is more suitable for chloride of silver gelatin plates than that recommended by Eder. It is also proposed to use it for developing dry collodion plates prepared with emulsion or in the silver bath, and for bromide of silver gelatin plates. It is unnecessary to add potassium bromide or chloride.

D. B.

**Value of Sulphurous Acid as a Disinfectant.** By G. WOLFF-HÜGEL (*Chem. Centr.*, 1882, 334–336).—The diffusion of sulphurous acid

in the air of the rooms in which these trials were made was found to be uniform, although in one or two cases there was a difference of 3 per cent. in the volume of gas at the ceiling and the floor of the rooms. The lime plastering of the walls had absorbed sulphurous acid in irregular quantities, and the diffusion of the gas on the objects to be disinfected and its penetration into them was unequal. The action of sulphurous acid as a disinfectant is said to be superficial, objects of large dimensions, *e.g.*, bales of goods, cannot be disinfected without loosening them and spreading the goods out.

In conclusion, it is mentioned that the experience as to the unsatisfactory penetration of sulphurous acid into objects to be disinfected is confirmed by the behaviour of micro-organisms. D. B.

**Salicylic Acid as an Antiseptic.** By E. ROBINET and H. PELLET (*Compt. rend.*, **94**, 1322—1324).—As the result of a large number of experiments with wines, worts, &c., the authors conclude, contrary to the statement of Girard, that in quantities of 0.5 gram per litre salicylic acid is an efficient antiseptic. 0.2 gram per litre prevents the fermentation in wines to which sugar has been added. 0.3 gram per litre retards considerably the fermentation of sweet worts. 1.0 gram per litre prevents the action of yeast. After some time worts yield a deposit which contains salicylic acid. Generally, for quantities of 0.5 gram per litre, the clear liquid retains 0.3 to 0.35 gram, the remainder being in the precipitate. Moreover, when wines containing salicylic acid are kept in casks, the wood absorbs the acid gradually, and retains it with great tenacity. C. H. B.

**Preservation of Must by Means of Salicylic Acid.** By J. BERSCH (*Bied. Centr.*, 1882, 340).—The retarding action of salicylic acid on fermentation commences when  $\frac{2}{2000000}$  to  $\frac{1}{2000000}$  are present, whilst  $\frac{11}{2000000}$  is sufficient to suppress the fermentation wholly. These figures are only applicable to freshly pressed must. The influence of the acid is overcome by the addition of fresh yeast, and exposure in open vessels. E. W. P.

**Tincture of Iodine.** By J. CASTHELAZ (*J. Pharm.* [5], **5**, 498—499).—Advantage is taken of the oxidation of hydriodic acid by potassium iodate to counteract the reduction which takes place when tincture of iodine is kept.

To every 130 grams of tincture of iodine of the codex (120 grams alcohol 90° and 10 iodine) 1 gram potassium iodate is added, which is capable of reducing 3.58 grams hydriodic acid with the formation of 3.56 grams iodine, or more than one-third of the total iodine present. The proportion of iodine is thus always kept constant. The maximum quantity of potassium iodide which can be formed, 0.59 per cent., is so small as not to interfere with the action of the tincture, and therefore may be neglected. Potassium periodate may be substituted for potassium iodate. L. T. O'S.

**Behaviour of Nitrogen Tetroxide (Hyponitric Acid) with Sulphuric Acid.** By G. LUNGE (*Ber.*, **15**, 488—495).—Lasne and

Benker have lately patented a process for reducing the loss of nitre in the manufacture of sulphuric acid, founded on the following assumptions:—1. That as the gases escaping from the chamber contain at least 5 per cent. of oxygen, therefore all the nitrogen compounds must be present as the peroxide. 2. That the liquid “nitrose” running from the Gay-Lussac tower does not contain any peroxide, because the latter forms only a very feeble combination with 1.75 sulphuric acid, and is easily driven off by a stream of air or carbonic acid, especially when the temperature is slightly raised; it therefore passes off unabsorbed into the air; this, in their opinion, constitutes the great loss of nitrogen compounds in the sulphuric acid manufacture. 3. They account for the presence of nitrous anhydride in the “nitrose” from the fact that the sulphurous acid which is mixed with the gases escaping from the chamber reduces some of the  $\text{N}_2\text{O}_4$  to  $\text{N}_2\text{O}_3$ ; their process consists in passing into the bottom of the Gay-Lussac tower a sufficient quantity of sulphurous acid mixed with steam to convert all the  $\text{N}_2\text{O}_4$  into  $\text{N}_2\text{O}_3$ .

With regard to these statements the author points out, firstly, that he proved experimentally (*Ber.*, 12, 357, and *Dingl. polyt. J.*, 223, 63) that  $\text{N}_2\text{O}_3$  can exist as a vapour in the presence of a large excess of air. Secondly, that  $\text{N}_2\text{O}_4$  is not absorbed as such by sulphuric acid, but that the absorption takes place thus:— $\text{N}_2\text{O}_4 + \text{SO}_2(\text{OH})_2 = \text{SO}_2(\text{OH})(\text{NO}_2) + \text{NO}_2(\text{OH})$ , and that the resulting liquid mixture of nitrosylsulphuric acid and nitric acid can be warmed on a water-bath for some time without suffering any loss of nitrogen, except when 1.65 sulphuric acid has been used as an absorbent, and even then the loss is very small. He confirms these statements by experiments in which he shows that  $\text{N}_2\text{O}_4$  is very readily and perfectly absorbed even by 1.71 sulphuric acid, and in fact he used two flasks for absorbing  $\text{N}_2\text{O}_4$  prepared from lead nitrate, the gas coming off at the rate of about two bubbles a second from a 5 mm. aperture, and found that the second flask had only  $\frac{1}{150}$  as much nitrogen compounds as the first; and even when the gas was passed into the already partially nitrogenised sulphuric acid at double the rate, a quite abnormal state of affairs, the second flask contained only  $\frac{1}{90}$  of the first, and only a mere trace escaped absorption altogether. The solutions were warmed in a water-bath for some time, but lost no nitrogen. Air was also drawn through for many hours, and the loss was then only very small, and could be accounted for as resulting from the dilution effected by the moisture of the air.

Thirdly, the author argues that the introduction of sulphurous acid, which is not a new idea (*see* Schwarzenberg; Bolley, *Handb. d. Chem. Zech.*, 2, I Grapp, 396), can be useful only in badly conducted works when too much air has been admitted; it then really amounts to conducting part of the chamber process in the Gay-Lussac tower. Excess of sulphurous acid must be avoided, or else, as the author has shown (*Ber.*, 12, 1060), it would denitrate the nitrosylsulphuric acid, producing nitrous acid and nitric oxide, which would escape into the air, thus occasioning loss. The author evidently does not think very highly of the process.

D. A. L.

**Manufacture of Nitre from the Salts of Osmose Water.** By the MARQUIS D'HAVRINGCOURT (*Bied. Centr.*, 1882, 299).—The average composition of the osmose water obtained in the preparation of molasses is—

KNO <sub>3</sub> .	KCl.	K <sub>2</sub> SO <sub>4</sub> .	Sugar.	H <sub>2</sub> O.	Insoluble matter.	Organic matter.
46.04	33.25	4.02	5.34	5.60	0.80	4.95

Nitrogen is present as nitric acid to the amount of 6.38 per cent. By concentration and purification, a manure, which contains 96 per cent. of the whole of the nitrate and 90 per cent. of the chloride, can be obtained.

E. W. P.

**Preparation of Basic Furnace-linings for Dephosphorising Pig-iron.** (*Dingl. polyt. J.*, 244, 150—153).—According to Jung-haug and Uelsmann, sodium or potassium carbonate is used instead of the corresponding chlorides. The durability of the lining is said to be increased by the addition of cryolite. The following is a modification of the usual method of preparing the lining. The raw or calcined masses of lime, dolomite, or magnesite, are ground and mixed with the flux. The mixture is then burnt to dust, and subsequently made into bricks, the dust being rendered plastic with tar treated with 3 per cent. flux. When the flux consists of carbonated alkalis, ground calcium phosphate, or bone-black, with addition of a few per cent. of the carbonated alkalis, is used for the preparation of basic bricks, muffles, &c. According to André the basic masses are burnt at a high temperature, then pounded and ground, the powder being formed into bricks by the addition of freshly prepared calcium sulphate. 2 per cent. of the latter forms a plastic substance. Borsig proposes to mix dolomitic limestone in a crude or calcined and finely divided form with 2—2.5 per cent. of crude boric acid, or 3 per cent. of fused powdered boracite. The mixture is used in a dry or wet condition for lining furnaces or for the preparation of bricks. According to the Society of Mines of Hörde and the Rhenish steelworks at Ruhrort, limestone free from magnesia, containing not more than 15—20 per cent. of silicic acid, aluminium oxide, iron oxide, and manganese oxide, may be used for the preparation of basic linings. The quantity of iron oxides should not exceed 6 per cent. It was further found that phosphorus passes into the slag without the “after blow” by the use of fluorspar equivalent to one-tenth part of tribasic calcium phosphate formed. Instead of fluorspar, alkalis, alkaline-earth or cryolite is used. The dephosphorisation is effected also by blowing air into a reverberatory furnace having a basic hearth. It is recommended to add, immediately before the introduction of the metal into the converter lined with basic bricks,—lime, or a mixture of 8 parts lime and 1 part ferric oxide. The mass is heated and air blown in for 6—10 minutes when the converter is emptied, and the metal treated with a mixture of 2—3 parts lime and 1 part ferric oxide free from silica. The quantity of flux in the first blowing amounts to twice the weight of silicon and phosphorus contained in the original charge, whilst the quantity used in the second operation depends on the durability of

the converter. The object of the addition of the second flux is to obtain a slag containing more than 36 per cent. of lime and magnesia. The basic flux may be replaced partially or wholly by manganese ores, cryolite, fluorspar, and caustic or carbonated alkalis, whilst phosphorite or bone-black mixed with clay or asphalt is used as lining. After the decarburation of the iron bath the oxidation of the remaining phosphorus is effected by the introduction of oxidising agents, *e.g.*, ferric and manganic oxides, into the iron. This operation takes the place of the after blow.

D. B.

**Solvents for Iodoform.** By VULPIUS (*Arch. Pharm.* [3], 20, 44).—Ethereal oils dissolve varying quantities of iodoform, the amount dissolved appears to increase with the percentage of oxygen in the oil. Benzene and petroleum spirit and chloroform solution become coloured after a short period. A more certain and definite preparation is obtained by dissolving 15 grams gelatine in 50 grams water and 7.5 glycerol, and to this when evaporated to 54 grams adding 27 grams alcoholised iodoform; this mixture is then to be cast in sticks, cooled, and hardened by ice, and the sticks when hardened are to be dried until they weigh two-thirds of their original weight. E. W. P.

**Purification of Commercial Alcohol.** By A. RICHE (*J. Pharm.* [5], 5, 480—490).—Several methods have been proposed for purifying those portions of the spirit which are impregnated with aldehyde and essential oils, and are severally contained in the first and last portions of the distillation of the crude spirit. The most notable is that of oxidation, but this is attended with the formation of acetic acid and ethyl acetate at the expense of the alcohol.

The process here described is one of reduction invented by Naudin and Schneider, who subject the crude alcohol to the action of a zinc-copper couple, when the hydrogen evolved acts on the spirit, deodorising it. In the case of alcohol prepared from beet-root, the spirit is also passed through a series of special voltameters. A description of the process would be incomplete without the diagrams which accompany the paper.

R. Pictet has also devised a method for the rectification of alcohol. The crude spirit is distilled in a vacuum in a boiler fitted with a rectifying column and inverted condensers, whereby the temperature is maintained as low as possible, and the less volatile products return to the boiler. The first products of distillation are collected in one receiver, and when the purer alcohol begins to distil, it is collected in a second receiver. This alcohol is almost pure, since the low-boiling aldehydes, &c., with which the crude spirit is associated, distil over between the temperatures of  $-10^{\circ}$  and  $+5^{\circ}$ . The alcohol thus purified is subjected to a further rectification in an apparatus connected with a condenser maintained at a temperature of  $-25^{\circ}$  to  $-50^{\circ}$  by liquid sulphurous anhydride.

The first portions are collected separately and re-rectified, the alcohol which afterwards distils being perfectly pure. By this process, pure alcohol is obtained at a very low cost.

Eismann treats the crude alcohol with ozone, by which the im-



purities are oxidised; a description of this process is reserved for a future communication.

L. T. O'S.

**Influence of the "Marc" on Wine.** By J. NESSLER (*Chem. Centr.*, 1882, 265).—By allowing the skins and stones of ripe grapes to remain in contact with the must, the resulting wine is said to improve in bouquet, &c., and is less liable to become stale and ropy. In order to redden wine with the skins of black grapes, the temperature of the wine should be between 15° and 17°. Bad grapes impart to white and red wines a brown colour; such wines soon become turbid. Bad grapes and mildewed skins, as well as bad casks and puncheons, precipitate the red colouring matter, so that the wine becomes pale. The following are some of the cases in which the treatment of wine with "marc" has been successful:—

Wine which is muddy and cannot be clarified by the ordinary fining agents, wine in which a fining agent has been used which failed to sink to the bottom, wine which has become weak and flat, wine which is assuming or has assumed a black colour, wine having a barrel-taste or a by-taste, wine which is "corked," wine remaining after casking off, and wine which is obtained by pressing the lees. In cases where the fermentation of new wine has been checked suddenly the addition of "marc" prevents the separation of yeast. In order to improve the quality of inferior wines, it is proposed to keep them in casks which have been used for the following purposes. White grapes are freed from the stalks, crushed and brought into casks. The resulting wine is drawn off in the course of the following spring or summer, and the casks are then used for the above purpose.

D. B.

**Preservation of Wine by Means of Salicylic Acid.** By D. DENUÉ (*Chem. Centr.*, 1882, 265).—It is mentioned that the addition of 10—40 grams of salicylic acid to 1 hectolitre of pure wine is not injurious to health. It is useless to exceed this quantity, as larger additions of acid would be detected by the taste.

D. B.

**Preservation of Malting Barley.** By A. MÜNTZ (*Bied. Centr.*, 1882, 339).—The barley may be well preserved in so-called silos or upright vessels which are closed above and below with louvres capable of being opened at pleasure. The barley must be quite dry, and be stored during dry weather. The louvres must be regulated so as to allow of a slight change of air, which may be greater during the cold weather; but during warm damp weather they must be closed completely. The silos should stand in a sheltered position.

E. W. P.

**Preparation of Crude and Refined Milk-sugar.** By W. ENGLING and E. RÜF (*Bied. Centr.*, 1882, 346).—According to the present modes of obtaining milk-sugar, a considerable loss is incurred by the conversion of part of the sugar into uncrystallisable lactose; this change is occasioned by the presence of free lactic acid and potassium hydrogen phosphate in the whey. To avoid this loss, 50—100 grains chalk are to be added to every 100 litres of the whey (freed from lactoproteids), and the whole evaporated to one-half its original

bulk; the phosphates, &c., then sink to the bottom, and the supernatant liquid on further evaporation yields fairly pure sugar. Cold may also be employed, which by forming ice leaves a strong solution of sugar. It is also advisable, because of the higher value of pure milk-sugar, to refine it, which is accomplished by adding aluminium sulphate and chalk; the precipitate thus formed removes all colouring matters. The evaporated solution yields a crop of crystals, and after their removal alcohol is to be added, which causes a further precipitation.

E. W. P.

**Preparation of Strontium Saccharate from Molasses and Syrup.** By C. SCHEIBER (*Chem. Centr.*, 1882, 265).—In a patent taken out by the author he describes (1) the production of strontium saccharate in molasses liquors; (2) its separation from the non-saccharine ley; (3) the decomposition of the saccharate into crystals of strontium hydroxide and sugar solution containing strontium by cooling; (4) the separation of the crystals of strontium hydroxide from the sugar solution; (5) the saturation of the latter with carbonic anhydride, the separation of strontium carbonate by filter-pressing and the after-saturation; (6) the working up of the juice obtained from the presses; (7) the saturation of the non-saccharine leys obtained in operation (2) with carbonic anhydride for the recovery of the strontium oxide contained therein, and utilisation of the non-saccharine leys when free from strontium; (8) the burning of the strontianite and of the bricks of strontium hydroxide for the recovery of strontium oxide; and the slaking of the latter to obtain crystallised strontium hydroxide  $\text{Sr}(\text{OH})_2 + 8\text{H}_2\text{O}$ .

D. B.

**Improvement in the Manufacture of Sugar from Molasses by Means of Lime.** By L. BODENBENDER and others (*Bied. Centr.*, 1882, 348).—Bodenbender describes a mixing machine consisting of a double walled cylinder, in which two axles fitted with blades rotate so as to mix all thoroughly. Steam or cold water is introduced into the outer chamber so as to regulate the temperature. Steffens and Drucker state that in Steffens' process (*Abstr.*, 1879, 844) it is only necessary to cool the mixture down to a little below  $100^\circ$  before introducing fresh lime.

E. W. P.

**Extraction of Sugar from Lime Sludge.** By F. SCHILLER (*Chem. Centr.*, 1882, 264).—The author tried to extract the sugar from the lime sludge in the same way in which Scheibler effects the extraction of sugar from beet in his apparatus for estimating the amount of juice; 100 grams of mud are mixed in a mortar with 200 c.c. alcohol and filtered. The filtrate is diluted with 100 c.c. water, and the alcohol distilled off. The sugar solution thus obtained gave the following values:—Saccharose, 4.4; polarisation, 3.4; difference, 1.0; quotient, 77.2. Dry mud gave still better results. It was more difficult to carry on the extraction with Scheibler's apparatus. The same mud which, according to the above mode of treatment yielded a solution of 3.8 per cent. sugar per 100 g. mud, gave in Scheibler's apparatus only 2.1 per cent. Moreover the first experiment

lasted only one hour, whilst the second trial required three hours. The filtrate was then evaporated, and the mud re-treated with the condensed water. In six hours 1 k. dry mud was extracted with 100 c.c. of water in this manner. The solution was diluted to 200 c.c., and gave saccharose, 36.0; polarisation, 24.0; difference, 12.0; and quotient, 66.6. The same mud treated in Scheibler's apparatus with water, for an hour and a half, gave 100 c.c. of solution; saccharose, 26.0; polarisation, 1.62; difference, 0.98; and quotient, 62.3. The author considers this extraction method practicable on a large scale with proper apparatus. D. B.

**Substitute for Animal Charcoal.** By A. WACHTEL and E. E. SCHOTT (*Bied. Centr.*, 1882, 349).—Mountain cork containing about 94.2 per cent.  $\text{SiO}_2$ , is dried, ignited, and soaked in molasses, then dried and ignited; this latter part of the process is repeated, until a mass containing 3.5 per cent. carbon is obtained. This substitute acts efficiently on the removal of colour from molasses, but is not quite so good as charcoal, but it removes a larger portion of the alkalis. Schott recommends heating a mixture of porous peat and bituminous coal together; the resulting mass is efficient as a decoloriser and disinfectant. E. W. P.

**Oleic Soap.** (*Chem. Centr.*, 1882, 272.)—This soap is used chiefly for fulling purposes. Its manufacture is different from that of other hard soaps, as owing to the rapidity with which the saponification is effected, the greater part of the ley must be in the copper before the oleic acid is added. Oleic acid, like rosin, works best in carbonated leys: hence in preparing oleic soap ash leys of 20–50° B. are used. The saponification is effected in the following manner:—2000 lbs. ley of 20° B. are run into the copper, and when this boils 1000 lbs. oleic acid are added, stirring the mixture constantly. 500 lbs. oleic acid, and 700 lbs. soda-ley (20° B.) are then introduced in successive portions. When the saponification is at an end, common salt is added. The soap is now boiled until it becomes clear. It is then kept at rest for 12–18 hours in the covered copper, after which it is poured into the frames. The resulting product exhibits a silvery appearance, is firm, and has an agreeable smell. D. B.

**Scherff's Process for Preserving Milk.** By B. MARTINY (*Bied. Centr.*, 1882, 341).—By this process fresh milk enclosed in glass vessels, is heated for 1–2 hours to a temperature of 100–120° by superheated steam. All generators of fermentation are thus destroyed; the caseous albuminoids are peptonised, whereby the gastric juices only coagulate the milk in finely divided, easily digestible flocks; also any germs of disease, as tuberculosis, from which the cow may be suffering are destroyed. E. W. P.

**Is Milk Warmed by passing through the Centrifugal Machine?** By F. DANGERS and others (*Bied. Centr.*, 1882, 342).—Only a very slight rise of temperature has been observed; in Lefeld's machine a fall of 0.25° was noticed, and in Laval's a rise of 0.25°.

E. W. P.

## General and Physical Chemistry.

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**Absorption-spectrum of Ozone.** By J. CHAPPUIS (*Compt. rend.*, **94**, 858—860).—The paper contains a table giving the positions, in wave-lengths, of 11 bands, constituting the absorption-spectrum of ozone. The most characteristic of these bands are two between which falls the D line, and their respective limits are marked by the wave-lengths 609·5—593·5 and 577·0—560·0. By spectroscopic observation mere traces of ozone may be detected if a gaseous column of sufficient length be examined. R. R.

**Absorption-spectrum of Nitrogen Tetroxide (Pernitric Anhydride).** By J. CHAPPUIS (*Compt. rend.*, **94**, 946—948).—When nitrogen is introduced into the oxygen intended for the preparation of ozone, a compound of oxygen and nitrogen is formed, which gives a peculiar absorption-spectrum of fine dark lines. The positions of eight of these are given in the paper, the most characteristic lines being one corresponding to the wave-lengths 668—665, and another at 628—625. R. R.

**Colour of the Mediterranean and other Waters.** By J. AITKEN (*Proc. Roy. Soc. Edin.*, **110**, 472—483).—The experiments were made with a view of determining whether selective reflection or absorption was the cause of the blue colour of water. Three different methods were adopted, and all three proved that the colour is due to selective absorption. A long tube closed at the end with a glass plate was sunk vertically in the water; as seen through this tube white objects appeared blue. In the second method a white object was looked at through a tube blackened internally and filled with water; the water was found to absorb the red rays. The third method was to sink white and different coloured objects under water; then the white changed to blue; the red darkened, a very small depth of water sufficing to destroy the colour; yellow changed to green; purple changed to dark blue or violet. If the colour of the water were due to reflection, then the test colours would all have appeared deficient in blue, and it is shown that under these circumstances white becomes yellow, and yellow deepens in tint. But selective absorption is insufficient to account for all the colour phenomena seen in water. The water of the Mediterranean has numerous fine solid particles in suspension, so that we have here both reflection and absorption occurring. By the first, all colours are reflected, and then the water by absorption strikes down the red rays, and only the blue are reflected to the surface. The solid particles determine the brilliancy, the absorption the colour. The colour of the particles in suspension influences the appearance of the water; thus yellow sand produces a green shade. In the Mediterranean the particles are whitish; when few particles

are present, the colour is deep blue, which becomes a chalky blue-green as the particles increase in number. It is from the shores that the white particles are obtained: hence after high winds and consequently greater attrition, the sea assumes a blue-green colour; the same reasoning accounts for the green colour close to shore, whilst further out blue is the prevailing tint. Examination of the waters of Lakes Como and Geneva, &c., showed that their remarkable colour arises from the same causes as already described. Loch Lomond presents an exception; a white surface submerged appears yellow, and the waters of this lake absorb most at the violet end of the spectrum. Careful preparation of distilled water shows that it is unnecessary to suppose the presence of impurities in water to account for its colour, as the colour is natural to it; but the addition of impurities affects the shade of blue. When light from clouds falls on water, the surface reflection is so strong as to mask the natural colour, whilst light from a blue sky is intensified.

E. W. P.

**Constitution of Solutions.** By G. KRUSS (*Ber.*, **15**, 1243—1249).

—The absorption-spectrum of a solution which contains two or more colourless substances, does not always correspond with the sum of the spectra of each substance taken separately, but often displacement, concentration of the bands, or even an entire derangement of the spectrum occurs. It has not yet been decided whether these phenomena are due to chemical decomposition within the liquid, or arise merely from physical causes; but recently the latter view has received the greater support. In order to examine this question, the author starts from the view that if the phenomena are due to physical causes, then the spectra will be the same, whether the light passes through solutions of the two substances taken separately, and of given concentration, or through a mixture of the two solutions of the same concentration mixed in the proportion 1 : 1, in a tube of double the dimensions. In the year 1876, Burger made a series of experiments on this point, but the author takes exception to the form of apparatus used, on account of the number of reflections involved, which cause a considerable diminution of the intensity of the light. The arrangement which the author adopted consists of two tubes, of internal width 5 mm., with parallel glass plates of about 2 mm. thickness (through which the light falls), which is designated by *a*. A comparison was drawn between the spectrum which resulted from the passage of the light through both these tubes placed parallel to one another, and each filled with a separate solution, and that formed when the light passes through a mixture of the same solutions mixed in proportion 1 : 1, through a tube of width 10 + *a* mm. Similarly, to compare three coloured substances three such tubes are taken, and the resultant spectra are compared. Thus taking the case of pararosaniline and picric acid, the former gives a strong absorption-band from  $\lambda$  570·4—518·2; and the absorption decreases to  $\lambda$  485, afterwards increasing from  $\lambda$  429·6; the latter gives a strong absorption-spectrum from  $\lambda$  483·8, towards the violet end of the spectrum. On placing the absorption tubes side by side, the same lines were observed, but on mixing the solutions the spectrum was altered, the absorption-bands  $\lambda$  570·4—

518.2 had disappeared, and there was a strong absorption from  $\lambda$  576.9 towards the violet, no colour being observable beyond  $\lambda$  483.8. In this case the alteration in the spectrum is dependent on a chemical change in the liquid, viz., a formation of rosaniline picrate, and not to physical causes. Similarly, the resultant spectrum of a mixed solution of cuprammonium sulphate and potassium dichromate is different from the spectrum of the two separate solutions, which points to a chemical change within the liquid. But mixed solutions of potassium mono- and di-chromate and of potassium permanganate and dichromate give spectra the same as the sum of the spectra of the two unmixed solutions. This method will be useful in indicating whether two or more dye-stuffs have any chemical action one on another, or can coexist without alteration.

V. H. V.

**Electrolysis of Distilled Water.** By D. TOMMASI (*Compt. rend.*, **94**, 948—951).—The author describes some experiments which he has made on the electrolysis of water, using silver or copper positive electrodes, and which he believes tend to show that, contrary to the prevalent opinion, water can be electrolysed, provided that the heat disengaged by the pile be at least equal to that absorbed by the decomposition of water into its elements (about 69 cal.).

R. R.

**Heat Developed by Magnetisation.** By PILLEUX (*Compt. rend.*, **94**, 946).—On passing the alternating currents from a De Méritens machine through an electro-magnet, the iron core became heated to 200°. Cores made of non-magnetic metals were not so heated, and the heating of iron and steel cores increased with their coercive force, which appears to play the same part as the electrical resistance does in a wire.

R. R.

**Specific Heat of Nitrogen Tetroxide.** By BERTHELOT and OGIER (*Compt. rend.*, **94**, 916).—The molecular specific heat (*i.e.*, referred to 46 grams) of nitrogen tetroxide, between 100° and 200° is + 17.4, which is higher than the sum of the specific heats of the constituent nitrogen and oxygen. Between 100° and 26°, the specific heat of nitrogen tetroxide is (contrary to what happens with all gases hitherto examined) much greater than between 200° and 100°. This is intelligible, as the heat of transformation is included, corresponding with the molecular work which gradually converts the nitrogen tetroxide from its theoretical density, agreeing with the formula  $\text{NO}_2 = 4$  vols. to a density nearly double.

R. R.

**Haloid Salts of Silver and Potassium.** By BERTHELOT (*Compt. rend.*, **94**, 912—916).—In this paper, the thermic phenomena attending the formation of double iodides, chlorides, and bromides are examined. The results show that the displacement of hydrochloric acid from its combination with oxide of silver by hydrobromic and hydriodic acids, free or combined with alkalis, readily takes place by reason of the thermic preponderance of these acids; and similarly the displacement of hydrobromic acid by hydriodic acid. These displacements would be exclusive if there were neither acid salts nor double salts.

These double salts render possible the inverse actions with potassium cyanide, which are then total and attended by re-solution of the chloride, bromide, or iodide of silver. This is explained by the heat of formation of the double cyanide, which is a salt stable in presence of water, and capable of being formed in totality.

With the alkaline chlorides, bromides, and iodides, the reactions are parallel to that of the cyanide; but the inverse actions are limited by the dissociation of the double salts. In all cases the results correspond with the thermic maximum.

R. R.

### Double Decompositions of the Haloïd Salts of Mercury.

By BERTHELOT (*Compt. rend.*, **94**, 760—765).—Here the author gives the results of the concluding experiments in his long investigation on the reactions between the haloïd salts of mercury, the haloïd acids, and the salts of potassium. The results of his researches on these reactions are thus summed up:—

*In presence of the haloïd acids*, the acid that develops most heat combines by preference with the mercuric oxide, without regard to the so-called affinities, or to solubility and insolubility; and the reaction is complete, provided no secondary compounds are formed, such as acid salts, acid hydrates, or double salts. But when the heat of formation of these secondary compounds exceeds the difference between the heats of neutralisation, then there is division of the acids; and this division is governed by different laws, according as it gives rise to soluble substances or to precipitates. In the former case, the action depends on the proportion between the quantities of the reagents present; in the latter, on the proportions existing at the contact of the liquid and the precipitate, in accord with the principle of *surfaces of separation*, and the rules laid down by Ditté.

*In the presence of alkaline salts*, the like considerations determine the reactions, for the system disengaging the greatest amount of heat is formed, whether the substances are soluble or insoluble. Thus Berthollet's laws are sometimes followed, sometimes contravened, according as they accord with thermochemical principles, or contradict them.

The above results hold good in the minutest particulars, and are accurately verified by the numerical determinations; they set aside all the hypotheses concerning coefficients of specific affinities, and accord in every respect with the principles set forth in the author's *Essai de Mécanique chimique*.

R. R.

**Expansion of the Alums.** By W. SPRING (*Ber.*, **15**, 1254—1257).—The author has made a series of determinations of the volumes and specific gravities of ammonium-, potassium-, cæsium- and rubidium-aluminium alums and of potassium-chromium alum. Apart from the consideration that the alums expand rapidly, about 60°, on account of an internal decomposition, the author, for the linear coefficient-expansion  $k$  between 0—60°, finds values varying between 0·0000246 and 0·0000267, which is within the limits of experimental error. This result of the quality of the expansion-coefficient values for the alums is in accordance with the well-known fact that large

crystals of one alum may be formed from the nucleus of another, to form compounds of varying composition. It is also probable that the alums have the same coefficient of compression; and if this hypothesis were correct, there should exist the same simple relation between isomorphous bodies which obtains among gases, *i.e.*, equal volumes of isomorphous bodies, under the same conditions, should contain the same number of molecules. In confirmation of this hypothesis, the author shows that the sp. gr. at  $0^{\circ}$  of the alums divided by their molecular weight gives a constant quotient within the limits of experimental error. This comparison between the physical properties of gases and isomorphous compounds is further borne out by the consideration, that two isomorphous bodies, like two gases, interdiffuse and mix together in every proportion without arriving at a point of saturation.

The author proposes to examine the properties of other isomorphous groups, in order to ascertain whether Avogadro's law is available for the determination of the molecular weight of solids. V. H. V.

**Ammonium Bisulphide and Ammonium Cyanide.** By ISAMBERT (*Compt. rend.*, **94**, 958—960).—In a mixture of hydrogen sulphide and ammonia gases, each gas exercises the same pressure, whether it be free or combined, and therefore the pressure of one of the gases is inversely as the pressure of the other. In a mixture of hydrocyanic acid and ammonia, the tensions of the hydrocyanic acid and of the ammonium cyanide regularly increase with the temperature; the tensions of the cyanide, in presence of an excess of hydrocyanic acid, are the same as those of hydrocyanic acid; and in presence of an excess of ammonia gas, the tensions of hydrocyanic acid follow the same law as that enunciated for ammonium sulphide. But the seeming confirmation of Engel and Moitessier's law is merely the consequence of a species of compensation; and in all cases we can draw just conclusions as to what occurs in a mixture of vapours of different kinds, only from the results of analysis. R. R.

**Law of Solubility of Carbonic Anhydride in Water at High Pressures.** By S. WRÓBLEWSKI (*Compt. rend.*, **94**, 1355—1357).

(i.) *The temperature remaining constant, the coefficient of saturation, i.e., the volume of gas (taken at  $0^{\circ}$  and 760 mm. pressure), dissolved in 1 c.c. water, increases less rapidly than the pressure, although tending towards a definite limit.*

(ii.) *The pressure remaining constant, the coefficient of solubility increases as the temperature decreases.*

These laws, which are supported by a table detailing the author's results, are not in accordance with the results of Khanikoff and Louguine, who found that under a pressure of four atmospheres the solubility increased at a slightly greater rate than the pressure, but this incorrect conclusion is due to a double error in the method of calculation employed. When this error is corrected, the results fully confirm the above laws. A certain relation exists between the laws of solubility and the formation of the hydrate  $\text{CO}_2 + 8\text{H}_2\text{O}$  (discovered by the author), which make it probable that the conditions for the formation of the hydrate  $\text{CO}_2 + \text{H}_2\text{O}$  can never be realised.



It is evident that a hydrate can only be formed under pressure when the water contains in solution a sufficient quantity of the gas to form that hydrate. In the case of  $\text{CO}_2 + 8\text{H}_2\text{O}$ , the coefficient of solubility  $S = 155$ ; at 30 atmospheres,  $S = 33.74$ , and on increasing the pressure, the gas liquefies, and the two liquids evaporate; but on lowering the temperature of the gas in contact with the water (probably until it reaches the temperature at which its solubility corresponds with the composition of the hydrate), the hydrate is formed, either on the sides of the tube where the layer of water is very thin, or at the *free surface* of the liquid, *i.e.*, where the decrease in temperature has taken place. It was impossible to convert a large volume of water into the hydrate, since it froze before the whole of it was saturated. It was therefore necessary to take a small drop of water and expose it over a large surface. For the formation of  $\text{CO}_2 + \text{H}_2\text{O}$ ,  $S = 1236$ , the pressure corresponding with this solubility (admitting the possibility of obtaining such a pressure) could only be obtained at a temperature so low that the probability is greatly in favour of the water freezing before it is reached.

The experiments were carried out in the apparatus described by the author (*ibid.*, 94, 954).

L. T. O'S.

**Absorption of Gases by Platinum.** By BERTHELOT (*Compt. rend.*, 94, 1377—1383).—*Absorption of Hydrogen.*—(1.) *By spongy platinum.* Spongy platinum absorbs several times its volume of hydrogen, forming a hydride which is not decomposed at a temperature of  $200^\circ$ , only 1 vol. of gas being expelled at that temperature. When oxygen in the cold is passed into the vacuous globe containing the hydride, water is formed, with evolution of 50 cal. per 16 grams oxygen, from which it may be deduced that 1 gram of hydrogen absorbed by spongy platinum and capable of being oxidised in the cold by free oxygen, evolves 9.5 cal. (2.) *By platinum reduced by formic acid.* The platinum thus prepared evolved no gas when heated in a vacuum to  $500$ — $600^\circ$ , and 62.55 grams absorbed 0.0342 gram hydrogen in the cold, with evolution of 14.2 cal. per gram of hydrogen absorbed, and formation of two hydrides: in a vacuum this loses 23 c.c. or 0.02 gram hydrogen, and on passing oxygen over it, the increase of weight is 0.0765 gram with development of 51.6 cal. per 16 grams oxygen, which is equivalent to 0.0091 gram of hydrogen. Consequently 0.0226 gram of hydrogen, or nearly two-thirds of the gas, remains as a hydride, which is not oxidised by oxygen in the cold. This hydride is decomposed by gradually heating it to the temperature at which glass softens. The heat of formation of the less stable hydride is + 8.7 cal.,  $\text{H} = 1$  gram, that of the more stable being nearly double, or + 17 cal. The proportion of the total weight of hydrogen absorbed to platinum = 1 to 20, while in the more stable hydride it is 1 to 30. (3.) *By platinum black.* This substance, prepared by the reduction of platinum in alkaline solutions, is always found to contain large quantities of oxygen as sub-oxides. The hydrogen absorbed is used partly in the reduction of the oxide, partly in the formation of hydride. The absorption of hydrogen in this case is attended with the evolution of + 12 cal. per gram of gas absorbed, but a small quantity of water

is formed at the same time. Of the hydrogen absorbed,  $\frac{1}{3}$ th is oxidised by oxygen in the cold, whilst  $\frac{2}{3}$ ths require a higher temperature.

*Absorption of Oxygen.*—The heat disengaged by the absorption of oxygen by the different forms of platinum is very small:—

Spongy platinum (117.6 grams) .....	0.0083 cal.
Platinum reduced by formic acid (66.3 grams) .....	0.0094 „
Platinum black heated in a vacuum to melting point of glass (72 grams) .....	0.0053 „
Black prepared at low temperature saturated with hydrogen, and then exposed to the air for some time (45.1 grams).....	0.0180 „

In calculating the small volumes to which these numbers correspond from the increase in weight of the platinum, the capacity of the globe and the density of platinum, very divergent results were obtained, being in some cases negative, showing that the sp. gr. of ordinary platinum differs from those of the black and other varieties. It may, however, be assumed that the heat evolved per equivalent of oxygen absorbed is considerable.

*Change of State of Platinum Black.*—The heat evolved when platinum black, heated to 200°, is treated with oxygen, decreases with the number of times it has been subjected to that temperature.

Black heated, once to 200° (95.9 grams) .....	= +0.0595 cal.
„ twice „ .....	= +0.0469 „
„ four times „ .....	= +0.0125 „
„ five times „ .....	= +0.0116 „

The volumes absorbed were so small that they could not be accurately determined, but the amount of heat evolved in the first case is about 92 cal. per gram. These results show that the platinum black undergoes a gradual change of state. Owing to the ready formation and instability of these hydrides and oxides, they play an important part in the reactions which take place in presence of platinum.

The electromotive force necessary to decompose water in presence of platinum is equal to the difference between the number of heat-units (cal. 34.5) absorbed in the separation of the hydrogen and oxygen, and the sum of those liberated in the formation of hydride (14.2 or even 17.0 cal.) and in the formation of the oxides, which, however, is unknown, but probably is very great, and this explains how the electrolytic indices are capable of measurement even with very feeble currents.

Owing to the various changes which take place both in the chemical constitution and conductivity of the electrodes, the reaction soon ceases. Thus the negative electrode which absorbs large quantities of hydrogen will act differently from the positive electrode, which absorbs only minute quantities of hydrogen.

Again, the ignition of a mixture of hydrogen and oxygen by platinum is due to formation of a hydride with liberation of heat, and its subsequent oxidation with a further development of heat, and these

two reactions continue and raise the temperature until finally it is sufficiently high to ignite the gaseous mixture. L. T. O'S.

**Relation of Molecular Volume to Atomic Combination.** By R. SCHIFF (*Ber.*, 15, 1270—1274).—This paper is a preliminary communication on molecular volumes, based on the author's method of determination of the specific gravity of liquids at their boiling points. Buff has previously supposed that the atomic volume of carbon in organic compound varies with the degree of valency. The author considers that Kopp's values,  $C = 11$ ,  $H = 5.5$ , must be considered merely as averages, and among fifty substances examined he cites only four cases in which the difference between the found and calculated values was one unit or less. The atomic volume of carbon varies not only with the degree of quantivalence, but also, the quantivalence being the same, with the method of combination. The results of the authors show that in the *fatty* series the normal compounds have, with higher boiling point, lower sp. gr. and larger molecular volume, but the secondary compounds have with lower boiling point higher sp. gr. and smaller molecular volume; whilst in *aromatic* compounds the normal compounds have lower boiling point, higher sp. gr., and smaller molecular volume, but secondary compounds have higher boiling point, lower sp. gr., and larger molecular volume. Thus the normal substances of one series are comparable with the secondary compounds of the other. Following this rule, it is found that two comparable substances, of which the first contains four hydrogen-atoms more, and two carbon-atoms less than the second, possess equal molecular volumes; as for instance the following pairs of substances:—

$$\left\{ \begin{array}{l} \text{Normal hexane } C_6H_{14} = 139.7 \\ \text{Metaxylene .. } C_8H_{10} = 139.7 \end{array} \right\} \left\{ \begin{array}{l} \text{Secondary hexane} = 138.7. \\ \text{Ethylbenzene ..} = 138.9. \end{array} \right.$$

A comparison of series of saturated compounds, which contain an equal number of carbon- and a variable number of hydrogen-atoms, shows that the atomic volume of hydrogen is 5.6. The volume difference for one or more so-called double bonds can be ascertained either (1) by a comparison of two saturated and one unsaturated compound which contain the same number of carbon-, but variable numbers of hydrogen-atoms, or (2) by a comparison of a saturated and unsaturated compound which differ from another by 2H.

Thus according to (1) by comparison of diisobutyl,  $C_8H_{18}$ , caprylene,  $C_8H_{16}$ , and ethyl-benzene,  $C_8H_{10}$ , the value of the double bond is 4.07. According to (2) by comparison of normal propyl and allyl alcohol the value of the double bond is 4.10. A series of such examples shows that each so-called double bond or every "deficit" raises the atomic volume by about 4 units, a result which agrees with the view that the double bond is a looser form of combination than the single bond (cf. Brühl, this vol., 446).

V. H. V.

**Affinity Value of the Silicofluorides of the Metals, as Deduced from the Law of Smallest Volumes.** By W. MÜLLER-ERZBACH (*Ber.*, 15, 1301—1303).—The author has examined the

silicofluorides, in order to determine whether the most electropositive element, cæsium, follows the law that the elements tend to arrange themselves ultimately in those forms of combination which occupy the smallest volumes (cf. this vol., pp. 137 and 451). From this law of smallest volumes the author finds that the metals with regard to the affinity-volumes of the complex grouping  $\text{SiF}_6$  follow the series Cs, Rb, K, Na, Ba, which is identical with that deduced from a comparison of other compounds of these metals. This confirms the observation of Gottenberg on the strong affinity of cæsium for oxygen, and those of Bunsen and Kirchhoff, which showed that rubidium amalgam was electropositive to potassium, but electronegative to cæsium amalgam.

V. H. V.

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## Inorganic Chemistry.

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**Numerical Results of the Mean Ratio of Oxygen to the Sum of Oxygen and Nitrogen in Atmospheric Air.** By E. W. MORLEY (*Chem. News*, 45, 283).—Since the proportion of oxygen to nitrogen in the air varies almost as incessantly as its temperature or pressure, the mean value can be accurately ascertained only by regular and continuous observation. A series of daily analyses in duplicate, continued for six months, although undertaken for a very different purpose, is therefore of some interest as contributing to the knowledge of this constant. The result is affected with errors, depending on the following causes :—

1. The most serious uncertainty depends on the uncertainty of the calibration of the eudiometer. The probable error of the mean result is 0·0014 per cent.

2. The second source of uncertainty depends on the fact that the composition of the air is variable. Owing to this variation, the result of the number of samples analysed is as likely as not to differ from the result from an unlimited number of samples by 0·0009 per cent.

3. The third source of uncertainty depends on the accidental errors of analysis. The probable error is 0·0002 per cent. This result is also affected with one source of error, which has not yet been taken into account. It is due to the fact that the eudiometer tube after the explosion contains a larger volume of water than at the previous measurement. The author does not see clearly how to determine the magnitude of this error.

The mean composition of the air and the magnitude of the errors attending the determination may be stated as follows :—

Ratio of oxygen to sum of oxygen and nitrogen..	20·9490	per cent.
Probable error from imperfect calibration .....	0·0014	„
Probable error from variation in ratio.....	0·0009	„
Probable error from accidental errors .....	0·0002	„
Total probable error .....	0·0016	„

D. B.

**Some Conclusions as to the Cause of the frequent Fluctuations in the Ratio of Oxygen to Nitrogen in the Air at different Times.** By E. W. MORLEY (*Chem. News*, 45, 284).—The author has made duplicate analyses of air collected at Hudson, Ohio, on every day, from January 1st to June 30th, 1880, and has been furnished with the thrice-daily maps of the state of the weather for the same interval. From a comparison between these maps and the results of his analyses, the author deduces some interesting conclusions, serving to confirm the notion that most of the variations in the amount of oxygen are caused by the vertical descent of air from above. He finds this notion strikingly confirmed in some cases, in which he was formerly of opinion that Loomis' suggestion that the cold was caused by the descent, could not be admitted. It was found that some depressions of temperature are caused by such descent, and at such times the amount of oxygen falls promptly at the beginning of the cold. But with the times of depression of temperature remarkable for their suddenness and severity, a vertical descent of cold air seems to be the effect and not the cause. The descent follows the cold by a day or two or more, and at the time when the signal service maps lead the author to suppose the descent has begun, and not till then, the fall in oxygen occurs.

D. B.

**Amount of Carbonic Anhydride in the Atmosphere at Calèves, near Nyon, Switzerland, Altitude 420 m.** By RISLER (*Compt. rend.*, 94, 1390—1391).

Volumes in 10,000.			
	Mean for month.	Maximum for month.	Minimum for month.
1872. August ..	2.998	3.492 on 9th	2.616 on 2nd.
September ..	3.020	3.123 „ 12th	2.530 „ 5th.
October ..	2.953	3.067 „ 25th	2.793 „ 20th.
November ..	3.043	3.204 „ 15th	2.867 „ 1st.
December ..	3.058	3.215 „ 11th	2.919 „ 17th.
1873. January ....	3.016	3.094 „ 29th	2.889 „ 30th.
February....	3.045	3.196 „ 28th	2.820 „ 20th.
March .....	3.088	3.239 „ 26th	2.914 „ 20th.
April .....	3.053	3.261 „ 1st	2.861 „ 28th.
May .....	3.139	3.336 „ 3rd	2.880 „ 25th.
June.....	3.062	3.318 „ 8th	2.653 „ 22nd.
July.....	2.944	3.128 „ 1st	2.665 „ 7th.

Annual value 3.035

L. T. O'S.

**Composition of Hydrated Carbonic Acid.** By S. WROBLEWSKI (*Compt. rend.*, 94, 954—958).—The experiments described in this paper lead the author to conclude that at the temperature of 0°, and under the pressure of about 16 atmospheres, carbonic anhydride unites with water to form a hydrate of the composition  $\text{CO}_2 + 8\text{H}_2\text{O}$ .

R. R.

**New Method of Preparing Hyponitrous Acid.** By W. ZORN (*Ber.*, 15, 1258—1259).—The methods of preparing hyponitrous acid by the reduction of sodium nitrate or nitrite with sodium amalgam, or by the electrolysis of these salts with mercury as a negative electrode, are costly, and involve a considerable expenditure of time. The author finds that the method proposed by Menke (this Journal, 1878, 401), which consists in melting sodium nitrate with iron filings, yields no hyponitrite. It is shown in the present paper that freshly precipitated ferrous hydroxide reduces nitrates and nitrites readily. Silver hyponitrite may easily be obtained by this means. Ferrous sulphate is precipitated with milk of lime; the thick paste of ferrous hydroxide and calcium sulphate is then added to a solution of sodium nitrite, and the whole mixture is left in a cool place; the solution is filtered; and the filtrate, after neutralisation with acetic acid, is precipitated by silver nitrate, which throws down pure silver hyponitrite. From 1 kilo. ferrous sulphate and 100 grams nitrite, about 10 grams of the silver salt were obtained. V. H. V.

**Hydrate of Hydrogen Sulphide.** By DE FORCRAND (*Compt. rend.*, 94, 967).—A crystallised hydrate of hydrogen sulphide is formed under a pressure of 17 atmospheres at ordinary temperatures, but at 30° it is decomposed, even under considerable pressures. When the pressure exceeds 23 atmospheres, the gas entirely disappears, and the tube contains only two liquids, which cannot be made to combine by pressure. This hydrate has not therefore a fusing point proper, but there is a critical point of decomposition at about 30°. From the results of some preliminary attempts at determining its composition the author is inclined to regard it as  $\text{H}_2\text{S}, 15\text{H}_2\text{O}$ . R. R.

**Solubility of Sulphurous Oxide in Sulphuric Acid.** By J. T. DUNN (*Chem. News*, 45, 270—272).—The author, having determined the solubility of sulphurous oxide in concentrated sulphuric acid at the ordinary temperature, thought it desirable to extend the determinations to other temperatures and to other strengths of acid. In the first place the solubility in concentrated acid at different temperatures was determined, making use of the apparatus described by Bunsen in his "Gasometry" with a very slight modification. A large test-tube was fitted with a cork pierced by three holes; through the first a thermometer was inserted; through the second passed the tube from the  $\text{SO}_2$  supply down to the bottom of the test-tube; and through the third passed a glass tube bent twice at right angles, which served as exit-tube for the superfluous gas while the saturation was going on, and by simply pushing it down through the cork until it dipped beneath the acid, was converted into a delivery-tube for the saturated acid. In this apparatus was placed about 50 c.c. of the acid to be saturated, and the whole was then placed in a large beaker of water, which could be kept at any temperature by the help of a Bunsen burner and an electric thermostat. A moderately rapid current of sulphurous oxide prepared from copper and pure sulphuric acid, and carefully dried, was now passed through the acid in the apparatus for a length of time sufficiently great to insure the complete saturation of

the acid. The exit-tube was now pushed down into the acid (and beneath the level of the  $\text{SO}_2$  delivery-tube, so as to avoid accidental entrance of bubbles into it), and the pressure of the sulphurous oxide still entering the vessel forced the liquid out through the tube. It was allowed to flow into a small stoppered bottle, the capacity and weight of which were known; the delivery-tube went to the bottom of the bottle, and the gas gradually and quietly displaced the air. When the bottle was full and had overflowed for some time, the delivery-tube was slowly withdrawn and the stopper immediately inserted. Thus a known volume of the saturated acid was obtained without any escape of sulphurous oxide; it was then weighed, and the sulphurous oxide determined by opening the bottle under a known quantity of standard solution of potassium dichromate, allowing time for the complete diffusion of the gas out of its bottle, and determining the unaltered dichromate by adding excess of standard ferrous sulphate and titrating back with potassium permanganate. In the next place the solubility in acids of different strengths at about the ordinary temperature was determined. A known quantity of the acid used was saturated in the apparatus originally used, and a weighed drying tube was attached to the exit-tube during the passage of the gas so as to catch any moisture carried off by the sulphurous acid. This tube was again weighed at the end of the trial, and from the gain in weight any alteration in the composition of the acid used could be easily calculated. The dilute acids used were prepared by mixing concentrated acids of 1.840 sp. gr. with water, and their composition was inferred from a determination of their sp. gr. The results which are tabulated in the original paper lead to the following conclusions:—The addition of water to sulphuric acid at first lowers the solubility coefficient. The coefficient diminishes rapidly on the addition of water so as to reach a minimum between  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ ; this minimum occurs probably at  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , for which acid the coefficient is little more than two-thirds of that for  $\text{H}_2\text{SO}_4$ . On the further addition of water the coefficient again rises rapidly, although not quite so rapidly as it fell, so that the solubility in  $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  is almost the same as that in  $\text{H}_2\text{SO}_4$ . Beyond this point the coefficient slowly rises with dilution.

In conclusion, the author mentions that it is interesting to note that not only does the minimum solubility of carbonic dioxide correspond in position with that of sulphurous acid, but the proportion which the minimum coefficient bears to that for sulphuric acid is nearly the same in both cases.

D. B.

**Boiling Point of Zinc.** By L. TROOST (*Compt. rend.*, **94**, 788).—The author, referring to a paper published by Violle, calls attention to the fact of his having, in 1863, determined the boiling point of the zinc of commerce, and found it to be  $942^\circ$  as the mean of 27 experiments.

R. R.

**Cuproso-cupric Sulphites.** By A. ÉTARD (*Compt. rend.*, **94**, 1422—1425).—Chevreul's salt,  $\text{Cu}_2\text{SO}_3 \cdot 2\text{H}_2\text{O}$ , does not unite with sodium bisulphite, but by mixing it with a solution of the bisulphite (sp. gr. 1.26) and exposing it to the action of the air to oxidise the



cuprous sulphite, a yellow precipitate is formed, consisting of prisms having the composition  $\text{Cu}_{12}\text{Na}_8\text{S}_{14}\text{O}_{43} + 18\text{H}_2\text{O}$ , and a probable constitution  $\text{S}_8\text{O}_{32}(\text{Cu}_2)\text{Cu}''_2\text{Cu}''_8\text{Na}_8\text{H}_2\cdot\text{S}_6\text{O}_{24}\text{H}_{24} + 5\text{H}_2\text{O}$ , which is called *acid cuproso-cupric sodium octosulphite*. Sulphurous anhydride converts it into Chevreul's salt. It is as readily prepared by the partial reduction of cupric oxide by sulphurous anhydride as by the oxidation of salt rich in cuprous oxide. Thus it may be prepared by the reduction of cupric sulphate or acetate by sodium bisulphite.

By treating Chevreul's salt with excess of sodium bisulphite, or by acting on the yellow compound with sodium bisulphite, a dark red-brown compound is formed, crystallising in brilliant red leaflets with a metallic lustre resembling that of the platinocyanides. It has the composition  $\text{S}_8\text{O}_{32}\text{Cu}_4\text{Na}_8 + 9\text{H}_2\text{O}$ , and the probable constitution



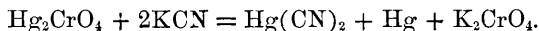
**Mercurous Chromates.** By P. and M. M. RICHTER (*Ber.*, 15, 1489—1492).—Normal mercurous chromate,  $\text{Hg}_2\text{CrO}_4$ , is converted by the action of alkalis into a black substance the composition of which, according to the authors' analyses, is represented by the formula  $3\text{Hg}_2\text{O}, \text{CrO}_3$ . The product of the reaction of mercurous nitrate and potassium monochromate is always the normal mercurous chromate, and not the compound  $4\text{Hg}_2\text{O}, 3\text{CrO}_3$ , as stated by Gmelin; the formation of a compound of this, or of any composition differing from the normal, is considered by the authors as due to impurities, probably to nitrite in the mercurous nitrate.

The action of ammonia on the chromates takes place in two directions, according to the solubility or insolubility of the hydroxides of their basyls.

(1.) In the former case the ammonia enters the molecule to form a crystalline metallammoniochromate, *e.g.*, Cu, Ni, Co, Ag, Zn, Cd.

(2.) In the case of metals whose hydroxides are insoluble in ammonia, *e.g.*, Pb, Fe, Hg, Au, Pt, Bi, U, Ce, Di, La, the ammonia simply decomposes the chromates, with formation of ammonium chromate.

The decomposition of mercurous chromate by potassium cyanide (solution) is represented by the equation—



When the mercurous salt is in excess, however, mercurous cyanide appears to be formed as a dark-green amorphous precipitate, but is very unstable. From the solution containing excess of potassium cyanide the double salt  $3\text{Hg}(\text{CN})_2, 2\text{K}_3\text{CrO}_4$  crystallises in plates, after a time. The mercury which is formed according to the above equation, is a black precipitate which may be employed for "silvering" glass; if it is spread over a glass plate and the water allowed to evaporate, a coherent film of metal is obtained. C. F. C.

**Action of Acid Solutions on Stannous Oxide.** By A. DITTE (*Compt. rend.*, 94, 792—794).—With regard to their action on stan-

nous hydroxide suspended in boiling water, acids may be divided into two classes, namely, those which form salts with stannous oxide entirely decomposable by boiling water, yielding crystallised stannous oxide, and those which form tin salts not decomposable by water or decomposable only with stable sub-salts, and never yield the anhydrous crystallised oxide. Salts of acids of the first class, if capable of decomposition by water with liberation of acid, behave like the acids themselves.

R. R.

**Action of Alkaline Solutions on Stannous Oxide.** By A. DITTE (*Compt. rend.*, **94**, 864—866).—With regard to their action on stannous oxide, alkaline solutions may be divided into two classes. Those of the first class, containing potassium, sodium, and barium hydroxide, transform the stannous hydroxide into anhydrous crystallised oxide, with accompanying phenomena of a more or less complex character. The second class, of which ammonia is an example, do not sensibly dissolve, or in any way act on stannous hydroxide.

R. R.

**Dimorphism of Stannic Oxide.** By M. LEVY and L. BOURGEOIS (*Compt. rend.*, **94**, 1365—1366).—By fusing 1 part of stannic oxide with 4 parts sodium carbonate at a bright-red heat in a platinum crucible, and treating the fused mass with dilute nitric acid, fragile hexagonal plates are obtained (sp. gr. 6·7) of a more or less yellow colour, somewhat resembling mosaic gold. They are attacked by acids with difficulty, although more readily than the crystals of zircon (*ibid.*, **94**, 812). On analysis, the following results were obtained:—

Sn.	Pt.	O.	
51·94	22·48	19·58	= 100·00.

The platinum was derived from the crucible, and the alloy of tin and platinum, obtained by reducing the oxide, contained the metals in the proportions required for the formula  $\text{Sn}_3\text{Pt}_4$ . It also contains 0·125 iridium. The hexagonal crystals, therefore, have the formula of cassiterite, and stannic oxide, like zircon, is dimorphous, and presents a crystalline form analogous to tridymite. The isomorphism of tin with platinum and zirconium is also proved.

L. T. O'S.

**Action of Alkaline Sulphides on Stannous Sulphides.** By A. DITTE (*Compt. rend.*, **94**, 1419—1422).—A solution of potassium sulphide, containing 20 per cent.  $\text{K}_2\text{S}$ , has but little action on stannous sulphide at the ordinary temperature, but more concentrated solutions act on it more quickly (according to their degree of concentration), with formation of potassium thioannate and metallic tin,  $2\text{SnS} + \text{K}_2\text{S} = \text{K}_2\text{S}_2\text{SnS}_2 + \text{Sn}$ : this is analogous to the formation of potassium stannate and metallic tin from stannous oxide and potassium hydroxide. This accounts for the reprecipitation of the tin as stannic sulphide after the addition of an acid to the alkaline solution. If the alkaline solution be very concentrated, a further reaction takes place; the potassium sulphide acts on the metallic tin, forming potassium thioannate and potassium hydroxide, and hydrogen is evolved,  $\text{Sn} + 3\text{K}_2\text{S} + \text{H}_2\text{O} = \text{SnS}_2, \text{K}_2\text{S} + 4\text{KHO} + 2\text{H}_2$ . Evolution

of hydrogen also takes place when metallic tin is heated with potassium sulphide. In presence of air, potassium sulphide is decomposed with formation of potassium hydroxide, the sulphur uniting with the stannous sulphide, forming stannic sulphide, which is dissolved by the potassium sulphide. Stannous oxide is also formed by the action of potassium hydroxide on the stannous sulphide. In concentrated solution, the stannous sulphide is decomposed, with formation of potassium thiostannate and metallic tin, whilst the potassium hydroxide formed holds the stannous oxide in solution as potassium stannate; but the presence of sufficient quantity of a potassium sulphide prevents the formation of stannous oxide.

L. T. O'S.

**Properties and Atomic Weight of Uranium.** By C. ZIMMERMANN (*Ber.*, 15, 847—851).—Chemically pure uranium can be prepared by heating in a closed iron crucible a mixture of sodium (3—4 parts), uranium tetrachloride (10 parts), and fused sodium chloride. If the crucible is brought to a white heat, the metal is obtained in compact masses. Uranium is a silver-white metal, softer than steel. It oxidises slowly on exposure to the air, and takes fire and burns when heated. In compact masses, it resists the action of nitric acid, but the finely divided metal dissolves easily. Hydrochloric acid readily attacks uranium. Mercury, silver, copper, tin, platinum, and gold are precipitated from their solutions by metallic uranium.

The specific gravity of uranium is 18·7, compared with water at 4°. The atomic volume is 12·8. The specific heat of the metal at 100° is 0·02765, and its atomic heat is 6·64 ( $Ur = 240$ ). The vapour-density of the volatile compounds and the specific heat of the metal confirm the accuracy of Mendelejeff's hypothesis, that the atomic weight of uranium is 240.

W. C. W.

**Action of Hydrogen Sulphide on Saline Solutions of Nickel and other Metals of the same Group.** By H. BAUBIGNY (*Compt. rend.*, 94, 961—963).—The author refers to the discordant statements which have been made as to the action of hydrogen sulphide on solutions of salts of nickel, cobalt, iron, zinc, &c. He asserts that under certain conditions, nickel, cobalt, and zinc may be completely precipitated from solutions of their chlorides and sulphates by hydrogen sulphide, and that iron may also be partially precipitated. Different experimenters, having operated under different conditions, have arrived at conclusions which are correct only for particular cases, and the results vary according to the dilution of the liquid; the nature of the acid of the salts; the proportions of acid and base; of free acid and water; the degree of saturation with the hydrogen sulphide; the temperature; and the duration of the experiment. These observations are illustrated by two comparative experiments with solutions of nickel acetate to which different proportions (60 : 1 and 20 : 1) of free acetic acid had been added. In 24 hours, nearly the whole of the nickel had been precipitated in the latter case, whilst in the former no change took place until after the lapse of several days, when the nickel began to precipitate very slowly.

R. R.

**Hydrogen Nickel Sulphide.** By H. BAUBIGNY (*Compt. rend.*, **94**, 1417).—The progressive formation of nickel sulphide when sulphuretted hydrogen is passed into a solution of nickel sulphate is shown to be due to the formation of a hydrosulphide. The analysis is carried out in a flask, into the neck of which are sealed two bulbs of equal capacities, and having a file mark on the neck of each. A solution of normal nickel sulphate is introduced into the flask, which is then saturated with sulphuretted hydrogen at  $0^{\circ}$ , and the flask sealed up. After the mixture has attained the surrounding temperature, the flask is inclined and the greater portion of the precipitate (absolutely free from sulphur) is received into one of the bulbs, together with some of the solution, whilst the clear solution is poured into the other, called the *test-tube*, taking care that it contains no trace of the precipitate. The temperature of the flask is then reduced to  $0^{\circ}$ , and the two bulbs broken off at the file mark and introduced into separate flasks containing fuming nitric acid, which are then sealed before the blow-pipe.

When the oxidation is complete, the sulphuric acid (due to the oxidation of sulphuretted hydrogen and to decomposition of sulphide and undecomposed sulphate) and nickel are estimated in the contents of each bulb, and from these data the quantity of undecomposed sulphate, and the proportion of nickel to sulphur in the precipitate, are obtained.

It was found that the quantity of free sulphuretted hydrogen in the contents of the *test-tube* corresponded exactly to that required by the coefficient of solubility of the gas in water at  $0^{\circ}$ , whilst that in the other bulb was in excess, and this is due to the formation of a hydrogen nickel sulphide; the proportion of hydrosulphide to normal sulphide varies, the maximum being about 14 per cent.

On repeating the same experiments with zinc sulphate, an excess of sulphur was found in the bulb containing the zinc sulphide. The author has shown that nickel sulphide acts on acid nickel sulphate in presence of sulphuretted hydrogen, whilst zinc sulphide under similar conditions does not; and inversely zinc sulphate in acid solution is not precipitated in presence of sulphuretted hydrogen by the sulphides which precipitate nickel. This difference can be due only to a difference between the combinations of nickel and zinc with sulphuretted hydrogen.

L. T. O'S.

**Action of Ozone on Manganous Salts.** By MAQUENNE (*Compt. rend.*, **94**, 795–797).—The precipitation of manganous salts by ozone is not so simple a reaction as is generally supposed, for experiments described in this paper show that it must be regarded as the result of a secondary action between the untransformed portion of the salt and the permanganic acid produced by immediate oxidation. This result is in accordance with thermochemical theory.

R. R.

**Basic Manganese Salts.** By A. GORGEU (*Compt. rend.*, **94**, 1425–1427).—On boiling a 20–25 per cent. solution of manganese sulphate with a 2 or 3 per cent. solution of soda, the white precipitate which is first formed is converted into a pink crystalline precipitate,

which is not decomposed by continued washing with water, remains unaltered when exposed to the air, and does not lose weight when heated at  $200^{\circ}$ . It appears to have the constitution  $3\text{MnO}, 2\text{SO}_3 + 3\text{H}_2\text{O}$ .

The *basic nitrate* is prepared by boiling a 60 per cent. solution of crystallised manganese nitrate with a concentrated soda solution, filtering, and allowing the filtrate to crystallise. It forms long slender brilliant needles, belonging to the rhombic system, which in dry air in the dark do not decompose, but in moist air and exposed to the light assume a brown colour. They decompose at  $100^{\circ}$  with evolution of water and nitric oxide, and at  $160$ — $170^{\circ}$  a residue of  $\text{Mn}_3\text{O}_4$  is left. Water decomposes the basic nitrate. It has the constitution  $2\text{MnO}, \text{N}_2\text{O}_5 + 5\text{H}_2\text{O}$ .

*Manganese oxychloride*.—By boiling a solution of manganese chloride in excess with a concentrated soda solution, a granular precipitate is formed, which does not oxidise in the air so readily as manganous hydroxide, and after long boiling with water, retains considerable quantities of manganese chloride. Different preparations did not give concordant results, but it appears to consist of 1 equivalent of  $\text{MnCl}_2$ , with 2 or 3 equivalents of  $\text{MnO}$ . The freshly prepared basic compounds dissolve in hydrochloric acid without evolution of chlorine.

L. T. O'S.

**Oxidation of Metals of the Platinum Group.** By T. WILLM (*Jour. Russ. Chem. Soc.*, 1882, 240—241).—The author finds that all the platinum metals, with the exception of platinum itself, when reduced by the action of hydrogen on their ammonio-chlorides or their ammonium compounds, undergo oxidation if heated to low redness in a current of air.

Palladium, rhodium, and iridium absorb oxygen with comparative facility, and are converted into the lower oxides. On heating pure palladium, prepared as above, in a current of air, the increase of weight is ultimately 6.68 per cent., and then remains constant. In this process palladium becomes converted into a homogeneous dark grey mass of the lower oxide  $\text{Pd}_2\text{O}$ , that formula requiring 6.99 per cent. of oxygen (found 6.68). On passing hydrogen at the ordinary temperature over the oxide, it is instantly reduced.

Metallic rhodium under similar conditions absorbs 12.96 per cent. of oxygen, and is converted into the oxide  $\text{RhO}$ , this formula requiring 13.29 of oxygen. According to Claus, the oxide of rhodium obtained by Berzelius and containing 18.07 per cent. of oxygen, which amount would correspond with the formula  $\text{RhO} + \text{Rh}_2\text{O}_3$ , was only a mixture of partially oxidised rhodium with ruthenium. A mixture of rhodium and ruthenium of such kind, is according to Claus, easily oxidised in the air, whereas, according to experiments of the same author, pure metallic rhodium undergoes scarcely any change. Iridium from chemically pure iridium-ammonium chloride absorbs 4.55 per cent. of oxygen. As the formula  $\text{Ir}_2\text{O}$  requires 3.88 per cent., and the formula  $\text{IrO}$  7.47 per cent. of oxygen, the compound in question is most probably a mixture of the two oxides  $\text{Ir}_2\text{O} + \text{IrO}$ , which would require 5.11 per cent. of oxygen.

The author is continuing his experiments.

B. B.

## Mineralogical Chemistry.

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**Contributions to the Petrography of the Philippine and Palau Islands.** By K. OEBBEKE (*Jahrb. f. Min.*, 3, 451—501).—Reference is made to previous literature. The present paper is an account of the specimens gathered by Semper. Microscopic and chemical examinations were made, and the various methods used to separate the constituent minerals for analysis are described, viz., the use of the electro-magnet, of hydrofluoric acid, and of Thoulet's solution.

*Amphibole-Andesite.*—(1.) From Limansana Islands. Brownish-green transparent hornblende and felspar (plagioclase) in large crystals; the two nearly equal in quantity. Secondary are light-green to colourless augite; the ground-mass consists of a dense mass of augite and felspar needles, with here and there crystallites and magnetic particles. A clear brown glass is present in varying quantity, but not abundantly. Apatite not rare. The rock is finely porous.

The felspar occurs in twins, single or polysynthetic, similar to albite, and also so that two systems of twins cross at 90°. Cleavage directions are unfortunately mostly absent. No section was observed showing the depolarising directions characteristic of sanidine; the felspar is therefore asymmetric. Small irregularly bordered felspars showed many and various enclosures, arranged concentrically or irregularly. The hornblende is always surrounded by magnetite, and is often converted into it entirely without change of form. The absorption and cleavage were those of hornblende, as also the depolarising angle  $c : t = 20-22^\circ$ . Twins as usual. The crystals showed a zonal structure, the dark zones having a depolarising direction inclined  $14^\circ$  to the normal direction of the lighter zones. Enclosures are few; the crystals are often broken, notched, &c.

The analysis of the rock gave—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.
54.48	19.44	1.80	4.90	7.08	3.72	3.58	3.32	1.70 = 100.02

The water probably belongs to a green chlorite-like substance contained in cavities in the rock, and perhaps to the glass. The silica is somewhat low, and the relation of potash to soda high, pointing to a felspar rich in potash. (2.) From Magalang, near Mt. Arayat. In appearance extremely like pumice-stone; colour pure white, with dark hornblende crystals: glassy plagioclase and dark mica plates form large enclosures. Microscopic magnetite crystals are present. The ground-mass is amorphous. The plagioclase is repeatedly twinned, shows a zonal structure, and contains as impurities only cavities with fixed bubbles. The crystals easily break out of the rock, and the optical examination offered several difficulties. Boricky's tests showed the presence of

much calcium, sodium, and a little potash. The felspar was isolated by solution of potassio-mercuric iodide solution, and obtained microscopically pure; sp. gr. = 2·641; the analysis gave the following ratios:—

$$\text{Al}_2 : \text{Si} = 1 : 4\cdot1; \text{Na(K)} : \text{Ca(Mg)} = 1\cdot8 : 1;$$

Rammelsberg gives for andesine—

$$\text{Al}_2 : \text{Si} = 1 : 3\cdot33 \text{ to } 1 : 4\cdot4; \text{ and Na : Ca} = 1 : 1 \text{ to } 3 : 1.$$

The sp. gr. is 2·641, somewhat lower than that of andesine, as given by Rammelsberg. It is therefore an andesine approaching in composition to an oligoclase. The hornblende is of a fine green colour, and has no magnetite surrounding it. The depolarising direction and pleochroism are those of hornblende; the crystals contain round or irregularly-shaped inclosures and cylindrical cavities, with an immovable bubble. The very brittle mica has a large axial angle. The ground-mass is a colourless or clear yellow glass containing innumerable gas pores. The rock may thus be described as a hornblende-andesine-pumice-stone. Various other localities are enumerated.

*Augite-andesite*.—Of the constituent minerals the plagioclase has exactly the same appearance and properties as that just described. Sanidine is but seldom present. The augite is light green, and generally pleochroic, viz.,  $b > a \geq c$ ; twin crystals are very frequent; enclosed are felspar, magnetite, glass (generally without), ashes, vapour-cavities, olivine, apatite, magnetite, tridymite, and hæmatite. (1.) From the Marivele peninsula. The rock is comparatively very light in colour, and often contains more or less hornblende. The rocks of this peninsula are to be divided into two groups—with and without hornblende. To the latter belongs a rock from the summit of the Sierra de Mariveles (3450 feet); it consists of a dense mass of small felspar crystals and rather larger shapeless augites; small octohedrons of magnetite are present, also strongly weathered particles, perhaps of augite or olivine. A glass basis is only occasionally present. The various enclosures of the ground-mass are also present in the plagioclase, but only to a very small extent in the augite crystals. In the plagioclase the twin lamellæ are not very numerous. The perfection of external forms of all the crystals has been more or less destroyed by the motion of the solidifying mass. The augite crystals show marked pleochroism. Both augite and felspar were isolated and analysed, as well as the rock itself. The ratio of  $\text{R}_2\text{O}_3 : \text{RO}$  in the strongly pleochroic augite is 1 : 15·5, the percentage of oxides being  $\text{Fe}_2\text{O}_3$ , 2·85;  $\text{Al}_2\text{O}_3$ , 3·71. In the felspar the ratios were found  $\text{Al(Fe)} : \text{Si} = 1 : 3\cdot1$  and  $\text{Na(K)} : \text{Ca(Mg)} = 1 : 1\cdot4$ ; hence it is labradorite, as is also shown by its sp. gr., which is 2·69. The loss on ignition of the whole rock is extremely slight, thus showing that the glassy constituent resembles obsidian.

The other rocks of Marivele, containing besides augite also hornblende, are evidently old lava streams; these two constituent minerals are both present as crystals. A rock from the south side of the bay contains also imbedded apatite, and intensely pleochroic hornblende crystals; the glass inclosures are very characteristic, and the small

cavities are frequently filled with minute tridymite crystals; the rock has undergone incipient decomposition. A rock from the north side of the bay has suffered considerable decomposition, the hornblende is entirely changed; the felspar contains very numerous enclosures, and is accompanied by calcite and zeolites; globular masses of chalcedony are present, and the rock contains 3·64 per cent. water.

(2.) From "Vulcan Taal." This smoking volcano, 600 feet high, forms an island in the deep sea of Laguna de Bombon. The north west is formed of an extinct conical volcano, Binintiang Grande. Numerous specimens were examined, mostly distinct augite-andesites, but many verging towards a basalt. They vary from very fine to coarse in structure, are often slag-like, and the cavities contain hæmatite, gypsum, and a mineral resembling breislakite. The principal mass of the crater is composed of a dense black rock, containing plagioclase, but little augite, glass, and magnetite. The plagioclase is labradorite. The ground-mass shows a fluidal structure. The quantity of magnetite is often very great. Some specimens are coloured red, with ferric oxide; in others the glassy constituent greatly predominates, and then contains inclosures of the above minerals; a few specimens contain olivine. All these rocks contain about 56—58 per cent. silica, and lose on ignition about 0·5 per cent., showing the glass to be an obsidian. The felspar from the rock of Binintiang was isolated and analysed; its sp. gr. (= 2·69—2·683), and composition  $\text{Al}(\text{Fe}) : \text{Si} = 1·3$  and  $\text{Na}(\text{K}) : \text{Ca}(\text{Mg}) = 1 : 1·4$ , both show it to be a labradorite.

(3.) From Mount Binay and the Mountains of South Batangas. The ground-mass is grey, and contains large crystals of plagioclase and augite; the rock is somewhat laminated, and is greatly weathered; it shows a fluidal structure.

(4.) From Albay Volcano. The lava of 1853 has been described as being a dolerite.

(5.) From Mount Arayat, in the plain of Pampagna. The rock from the north summit contains many enclosed pleochroic augite crystals, some felspar, and much olivine, in a very fresh condition. The rocks of the southern summit contain decomposed olivine.

(6.) From the Island, Mapua. One specimen closely resembles the preceding; it contains also a yellowish-brown to greenish-yellow fibrous substance, penetrating the plagioclase and augite crystals. Other specimens resembled those from Mariveles, which contain no hornblende and a large amount of glassy substance.

(7.) From Mount Pasian, Agusan. This deep-black rock contains imbedded felspar crystals up to 3 mm.; the glass shows in a remarkable degree a globular devitrification.

(8.) From Brook Dugang, tributary of the Rio Butuan. The glass shows signs of change, and the felspar crystals are also much altered, with formation of a chlorite-like substance.

(9.) From Shore of the Tipou, near Gosú. The stone is somewhat coarse in texture; it shows a fluidal structure. Many of the felspar crystals show no twin structure; the cleavage was not sufficiently distinct to allow of a correct determination.



(10.) From Cerro Negro, south-west corner of Mindanas. Closely resembles the preceding.

(11.) From the Island of Limansaua. The rock resembles the glassy ones from Mapua.

The rocks of Java, Sumatra, and Celebes show a remarkable resemblance to the above, and in all their variations. The author is of the same opinion as v. Drasche, that the products of eruption of the East Indian Islands and of the Philippines are the same, and all the volcanoes of these islands belong to the same system. Perhaps the augite- and amphibole-andesites of Japan have the same origin.

*Felspar-basalts.*—The felspar occurs almost exclusively in small lens-shaped crystals, with but few twin lamellæ; they show a fluidal arrangement. Large imbedded crystals fail; only their fragments are present. The augite occurs similarly. Olivine is present as large inclosures in large quantity; it occurs both fresh and more or less decomposed. The binding material is a brown glass. A green serpentine-like substance is probably an alteration-product of olivine. Magnetite is present in dense aggregates. The basalts of Isabela and the Island Lampinigan resemble each other. In appearance they are either greyish-blue, fine grained with a conchoidal fracture, or else blue-black, dense and with a splintery fracture. The rocks of the Palau Islands are, according to Wichmann's account, augite-andesites, but the specimens from the south coast near Rallap, examined by the author, are felspar-basalts. In appearance they vary much, being very dense and fine, or containing many and large imbedded crystals, or having a decided mandelstein structure. The plagioclase is often much decomposed, the augite quite fresh, and the olivine both fresh and completely converted into serpentine; magnetite is very abundant. Occupying the cavities in the mandelstein are globular radiating masses of zeolite; pure specimens of this could not be obtained, but analysis showed that it greatly resembles thomsonite; analcime in crystals; calcite in crystals or fine veins; chalcedony, and a substance like delessite.

A rock from Cabayan, of the district Benquet, is a quartz-porphyrite. The imbedded felspar crystals, orthoclase, are mostly converted into kaolin; the ground-mass is extremely dense. A specimen from the Rio Agno, near Cabayan, is a quartz-diorite; both this and the preceding rocks contain compound growths of quartz and felspar. Pebbles from the Rio Maputi were found to resemble a coarse-grained gabbro, and a dense black slate. Pebbles from the Brook Dicanuni consist of plagioclase, augite minerals, and magnetite; they are probably norite. From the Brook Dicarön is a sample of olivine-rock. Specimens from Benquet and Ilocos Norte proved to be typical chloritic slates; they contained imbedded magnetite and hornblende crystals, and apparently also epidote. The so-called chalk of Bal-ou consists of radial arragonite.

H. B.

**Existence of Lithium and Boric Acid in notable quantities in the Dead Sea.** By DIEULAFAIT (*Compt. rend.*, 94, 1352—1354; comp. this Journal, 38, 17, and 40, 1019).—A further examination of numerous specimens of waters from the Mediterranean

Sea, Red Sea, Suez Canal, Chinese Sea, and the Indian and Atlantic Oceans, shows the widespread existence of lithium and boric acid in all these seas. This fact leads the author to the following hypothesis as to the origin of saline deposits in different soils:—"If a mineral water contains magnesium chloride, and at the same time lithium and boric acid in such quantities as to be readily detected in a few drops of the water, the water in all probability consists of a sea-water concentrated by evaporation; and in like manner when lithium and boric acid do not exist simultaneously in the water in appreciable quantities, it is absolutely certain that it is not the result, at least directly, of the evaporation of sea-water."

The water of the Dead Sea contains lithium in such quantities that its presence can readily be detected by means of the spectroscope in less than  $\frac{1}{1000}$  c.c.; 1 c.c. of the water also contains sufficient boric acid to show its presence when examined spectroscopically.

From the above hypothesis, it would seem certain that the waters of the Dead Sea are the residue of an inland sea, analogous to that of the Caspian Sea, or more particularly to that of the Karabaghaz, and has been separated from the ocean at some former time.

L. T. O'S.

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## Organic Chemistry.

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**Preparation of Propylene.** By F. BEILSTEIN and E. WIEGAND (*Ber.*, **15**, 1498—1499).—The authors recommend the following method of preparation of propylene, as giving better results than that of Le Bel and Greene (*Amer. Chem. J.*, **2**, 23), or that of heating propyl alcohol with sulphuric acid. Phosphoric anhydride (3 parts) is introduced into a capacious flask attached to an upright condenser, and propyl alcohol (4 parts) is allowed to drop from a separating funnel upon the mass. The flask is kept cool and repeatedly shaken, to prevent agglomeration of the anhydride. When some quantity of alcohol has been introduced, the remainder may be more quickly added, and the whole is lastly boiled until no more propylene is evolved. The gas is suitably purified, being allowed to pass, first, through a well cooled empty flask, whereby undecomposed alcohol is retained. The phosphoric anhydride decomposes the alcohol in the molecular ratio 3 : 4. The reaction proceeds smoothly and without blackening, and is to be recommended also for the preparation of the higher homologues of propylene. C. F. C.

**Propylene Bromide.** By F. BEILSTEIN and E. WIEGAND (*Ber.*, **15**, 1496—1498).—The authors have investigated the debromination of the isomeric propylene bromides by means of silver oxide. In the case of the unsymmetrical bromide, the chief product was propaldehyde,

no glycol being formed, and the course of the reaction would appear to be the formation of a monobromopropylene, and the conversion of this into the aldehyde, by simple exchange of Br for OH.

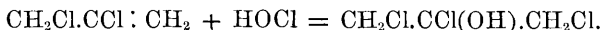
The normal bromide, on the other hand, exchanged both Br atoms for OH, the glycol  $\text{OH} \cdot \text{CH}_2\text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$  being the chief product of the reaction. A small quantity of acraldehyde appeared to be formed simultaneously, probably according to the equation:  $\text{C}_3\text{H}_6\text{Br}_2 + 2\text{Ag}_2\text{O} = \text{C}_3\text{H}_4\text{O} + 2\text{AgBr} + \text{Ag}_2 + \text{H}_2\text{O}$ . The reaction with silver oxide is shown, by these researches, to be capable of useful application to the diagnosis of bromides of this series. C. F. C.

**Action of Chlorine Dioxide on Hexylene.** By J. DOMAC (*Annalen*, **213**, 124—132).—The mixture of gases obtained by the action of potassium chlorate, oxalic acid, and dilute sulphuric acid, was passed into hexylene prepared from mannitol. The hexylene becomes yellow, but on exposure to the sunlight becomes colourless; the gases were passed into the hexylene until it remained yellow after exposure to sunlight. The product, on extraction with water, gave up to the water a small quantity of a mixture of acetic and butyric acids, leaving an oily liquid, which formed the chief product of the reaction. From the oil a compound was obtained which, on reduction, yielded secondary hexyl alcohol. It has not been found possible to determine the exact nature of this oil. P. P. B.

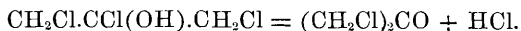
**Action of Hypochlorous Acid on Chlorallyl Chloride.** By L. HENRY (*Compt. rend.*, **94**, 1428—1430).—Hypochlorous acid acts on  $\alpha$ -chlorallyl chloride,  $\text{CH}_2\text{Cl} \cdot \text{CCl} : \text{CH}_2$  (b. p. 94—96°), less energetically than on allyl chloride, yielding:

(1.) Dichloracetone,  $\text{CH}_2\text{Cl} \cdot \text{CO} \cdot \text{CH}_2\text{Cl}$ , m. p. 42—43°, b. p. 171—172°.

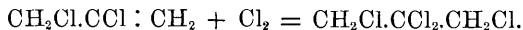
(2.) Allene tetrachloride,  $\text{CH}_2\text{Cl} \cdot \text{CCl}_2 \cdot \text{CH}_2\text{Cl}$ , b. p. 164—165°, a derivative of the hydrocarbon,  $\text{CH}_2 : \text{C} : \text{CH}_2$ , an isomeride of allylene, which the author has already proposed to name allene. It is insoluble in water, and is freed from traces of dichloracetone by shaking with sulphuric acid. It is probable that the reaction takes place in two stages. Firstly, the elements of hypochlorous acid enter the molecule of chlorallyl chloride, thus:—



But a body of this constitution is necessarily very unstable, and it splits up at once into dichloracetone and hydrochloric acid:



Secondly, the hydrochloric acid thus formed acting on a molecule of hypochlorous acid, liberates chlorine, which unites with a molecule of chlorallyl chloride, giving rise to allene tetrachloride—



From these facts is seen the influence of chlorine in a system having double linking in modifying the nature of the addition-products. By

the above method it is possible to obtain 50 per cent. of the chlorallyl chloride as dichloracetone, whereas Grimaux and Adam's method (*Bull. Soc. Chim.*, **36**, 20) yields only 15 per cent. of the dichlorhydrin employed.

L. T. O'S.

**Diagnosis of Tertiary Alcohols.** By C. HELL and F. v. URECH (*Ber.*, **15**, 1249—1251).—The authors have studied the action of bromine in presence of carbon bisulphide on various classes of organic compounds; in the case of the carboxyl acids it is supposed that bromine acts on the carboxyl group with formation of an acid bromide or anhydride, setting oxygen free, which is used up for the oxidation of the carbon bisulphide into acids of sulphur; but the primary and secondary alcohols give aldehydes and ketones without liberation of oxygen and formation of sulphuric acid. It seemed interesting to study this reaction with tertiary alcohols, in which two reactions are possible: either a ketone may be formed, thus:  $\text{Me}_3\text{C.OH} + \text{Br}_2 = \text{MeCOMe} + \text{MeBr} + \text{HBr}$ ; or an alcoholic bromide thus:



Experiment showed that in the case of trimethyl- and dimethylethylcarbinol the reaction is for the most part in accordance with the second equation, the liberated oxygen oxidising the carbon bisulphide. By this reaction, the tertiary may be distinguished in a most marked way from the primary and secondary alcohols.

V. H. V.

**Researches on *Tarchonanthus Camphoratus*.** By F. CANZONERI and G. SPICA (*Gazzetta*, 1882, 227—231).—This plant, belonging to the Composite order, sub-order *Asteroidæ*, is indigenous at the Cape of Good Hope. On exhausting its dried leaves with warm alcohol in a percolator, and leaving the alcohol to cool, a greenish-white gelatinous substance is deposited, which may be purified by washing it on a filter with alcohol as long as the filtrate exhibits a green colour, then drying it in the air, twice crystallising it from alcohol, washing the waxy substance thus obtained with ether, and finally crystallising it from alcohol.

The substance thus purified crystallises in white light scales, having a silvery lustre, melting at  $82^\circ$ , solidifying at a slightly lower temperature, and afterwards melting at  $72^\circ$ . It is tasteless, burns with a bright flame, leaving no residue, and emitting the characteristic odour of burnt wax. It is insoluble in water, slightly soluble in cold, freely in hot alcohol; not attacked by strong sulphuric or hydrochloric acid or by strong potash-ley, and not sensibly altered by fusion with potash. Its analysis gave, as a mean result, 83·66 per cent. carbon and 14·44 hydrogen, and the chloride obtained by treating it with phosphorus pentachloride gave 80·77 per cent. C, 11·12 H and 4·17 Cl. These results, together with the resistance of the substance to the action of melting potash, lead to the idea that it might be a higher homologue of myricyl alcohol,  $\text{C}_{32}\text{H}_{66}\text{O}$ , which is also unattacked by potash; if so it must contain 50 or more atoms of carbon, and might be represented by either of the formulæ,  $\text{C}_{50}\text{H}_{102}\text{O}$ ,

$C_{51}H_{104}O$ ,  $C_{53}H_{106}O$ . The corresponding chloride melts at  $67-68^{\circ}$ ; myricyl chloride at  $64.5^{\circ}$ .

It is not yet decided whether this alcohol, which the authors propose to call tarconyl alcohol, exists in the leaves in the free state or is produced by the action of the alcohol used in its preparation on a wax contained in the leaves. The solution from which the alcohol has been separated yields on evaporation a heavy, dark-coloured, pungent oil, consisting for the most part of an ether of an aromatic acid not yet examined.

H. W.

**Oxidation of Cane-sugar.** By C. HEYER (*Arch. Pharm.* [3], 20, 336—350, and 430—450).—*Oxidation by Chromic Acid.*—None of the notices on the oxidation of sugar by chromic acid give any quantitative data, merely stating that formic acid and carbonic anhydride are produced. The author has therefore investigated the subject quantitatively, and finds that besides formic acid and carbonic anhydride, oxalic acid is also formed. In an exact determination, the precipitated chromic oxide interferes, so that the solutions were always acidified with sulphuric acid. The action commences at ordinary temperature, but is hastened by the application of heat; and the rapidity of oxidation increases with the concentration of the solutions and amount of chromic acid employed. All experiments were therefore made with the same quantities of materials, in the same quantity of solution, and at like temperatures. The point to determine was whether all the three substances were produced at the same time or one after the other, the production of formic acid requiring 8 equiv. chromic acid, oxalic acid 12 equiv., and carbonic anhydride 16 equiv. The strength of the solutions was 1 equiv. of each in 1000 c.c. of water, and of the acid solution 8 c.c., 12 c.c., and 16 c.c., were used respectively. It was found that 8 equiv. were insufficient to completely oxidise 1 equiv. sugar, and that all three products were formed, the reaction being  $2CO_2 + 2CH_2O_2 + 2C_2H_2O_4$ ; with 12 equiv. acid (180) the reaction is,  $4CO_2 + 4CH_2O_2 + 2C_2H_2O_4 + 5H_2O$ ; in this case the completion of the reaction was aided by warming, but in a similar case, with the exception of the final heating, the reaction occurred thus:  $2C_{12}H_{22}O_{11} + 22CrO_3 = 4CO_2 + 10CH_2O_2 + 5C_2H_2O_4 + 11Cr_2O_3 + 7H_2O$ . In the third experiment the mixture (containing 16 c.c. sol. acid) was heated to  $120^{\circ}$ , with a considerable quantity of sulphuric acid; the chromic acid was completely reduced, having oxidised the sugar wholly to carbonic anhydride.

*Oxidation of Potassium Permanganate.*—The earliest notice on the oxidation of sugar by permanganate was made by Liebig and Pelouze, who found that oxalic acid and nothing further was produced, unless an excess of the oxidising agent was employed, and then the oxalates were converted into carbonates. Maumené afterwards thought that two new acids, hexepic,  $C_6H_{12}O_8$ , and trigenic,  $C_3H_6O_5$ , were formed. Heyer has repeated the experiments, employing a solution of sugar containing 1 equiv. in 2000 c.c. One equiv. sugar with  $4KMnO_4$  does not react completely in the cold, but if  $12KMnO_4$  is employed, and the mixture warmed, carbonic anhydride is produced, which forms the acid potassium salt, but no oxalic acid is produced.

Experiments with 6 and 8 equiv. permanganate yielded similar results, only the amount of carbonic anhydride produced was greater; when more than 8 equiv. were employed no reduction of the permanganate ensued. When 4 equiv. permanganate were allowed to remain in contact with the sugar for a long time at the ordinary temperature, oxalic and formic acids were produced in addition to carbonic anhydride, but it was only when 12 equiv. reacted that complete oxidation occurred; no other acids, as tartaric, could at any time be detected. The reaction therefore which occurs at a high temperature, is  $C_{12}H_{22}O_{11} + 12KMnO_4 = 6KHCO_3 + 6KHCO_2 + 12MnO_2 + 5H_2O$ .

The aid of heat may be dispensed with, if the solutions are concentrated, the reaction occurring unassisted. The action of permanganate is therefore as follows:—In dilute solutions at the ordinary temperature, formic acid, much oxalic and little carbonic anhydride; on the other hand, when the solution is warm and large quantities of permanganate in concentrated solutions are used, only formic acid and carbonic anhydride are formed; the higher the temperature and the greater the quantity and concentration of the solution, the greater the amount of carbonic anhydride produced. Maumené's experiments were repeated, and the solution after filtration was, as Maumené stated, no longer sweet, and was dextrorotatory, but this was due to the presence of potash salts, but inverted sugar was found also to be present. Oxalic acid is formed in the process, and this Maumené overlooked, or rather he considered the calcium oxalate to be a hexepate, and the lead hexepate is really a mixture of the oxalate and carbonate. As regards the supposed trigenic acid, the author thinks that it must have been a mixture of free acetic and formic acids with salts of potash, which was obtained by one of the processes of separation. Langbien's experiments were also repeated, and the influence of the presence of free sulphuric acid on the reaction was observed. When a sufficiency of acid is present, manganous salts, and not, as in the other experiments, manganese peroxides, were formed. Employing 5 equiv. sugar and 24 equiv. permanganate, 3 equiv. carbonic anhydride were evolved, and formic acid remained in solution, oxalic acid being absent; but the whole of the sugar was not reduced, there being an insufficiency of permanganate. In a second experiment 5 equiv. sugar and 48 equiv. permanganate ( $= C_{12}H_{22}O_{11} + O_{24}$ ) were heated at  $120^\circ$  for 2–3 hours; this caused complete oxidation, and formation of 12 equiv.  $CO_2$ . From these experiments we may conclude that the action of permanganate is similar to that of chromic acid; that the oxalic acid is formed only when the solution of permanganate is dilute and cool; that the action of permanganate is intensified by the presence of sulphuric acid, carbonic anhydride and formic acid being produced, but the latter is completely oxidised at higher temperatures and with a greater quantity of the oxidising agent.

E. W. P.

**Ethereal Nitrates from Milk-sugar.** By G. GÉ (*Jour. Russ. Chem. Soc.*, 1882, 253–260).—The products of the action of a mixture of nitric and sulphuric acids on lactose have been only superficially described by Reinchl and Vohl, and their statements contradict each other. In order to obtain the nitrates from lactose, the author proceeds

as follows. One part of milk-sugar is added in small portions, to five parts by weight of ice-cold fuming nitric acid (sp. gr. 1.5) and then two volumes of strong and cold sulphuric acid are added. The product of the reaction separates after some time and floats on the surface of the liquid, as a yellow, soft, waxy mass which soon becomes hard. It is then repeatedly ground in a mortar with the mixture of the acids, left in contact with them for some time, and finally washed well with water. The white amorphous powder obtained in this way is soluble in alcohol and ether, but insoluble in water, and consists of a mixture of two compounds. In order to separate them, the mass is placed on a filter and washed with cold alcohol of 80 per cent., until the filtrate becomes colourless. The compound remaining on the filter is the *lactose penta-nitrate*,  $C_{12}H_{17}(NO_2)_5O_{11}$ .—It is obtained after repeated recrystallisations from hot alcohol, in the form of semitransparent colourless scales which are easily reduced to a white powder. It is insoluble in water, but soluble in alcohol and ether. One part of the compound dissolves in 6.938 parts of boiling alcohol and 63.45 parts of alcohol of 16°. Its sp. gr. at 0° is 1.684, its m. p. = 139.2°. It begins to decompose slightly at 84°; at 135–140° it gives off yellow fumes and effervesces; and at 156° total decomposition with slight explosion takes place, and a brown mass is left behind. The air-dried substance does not suffer any loss of weight if heated at 75°, and, contrary to Vohl's statement, does not contain any water of crystallisation. It explodes when struck with a hammer on an anvil. *Lactose tri-nitrate*,  $C_{12}H_{19}(NO_2)_3O_{11}$ , is found in the yellow alcoholic filtrate from the penta-nitrate and forms, after the evaporation of the alcohol, a yellow mass of the consistency of bees-wax, which becomes hard and brittle at temperatures below 0°. On drying it for a long time over sulphuric acid in a vacuum, the compound loses 5 per cent. of water, becomes hard and is easily reduced to powder. In order to get rid of the last trace of acid, the compound is dissolved in alcohol, the solution poured into water, and this process repeated several times. It is only very slightly soluble in water, but very easily in alcohol and ether, either hot or cold, and the yellow solutions have a bitter taste. The compound cannot be obtained in crystals. Its sp. gr. at 0° is 1.479, its m. p. 36.86°; it is slightly decomposed at 90°, effervesces at 97°, gives off red-brown fumes at 107°, and decomposes totally at 110° with slight explosion.

If brought into contact with fresh quantities of sulphuric and nitric acids, it is converted into compounds containing a large number of the  $NO_2$ -groups. On exposing the ethereal solution of the products of reaction to a temperature of  $-25^\circ$ , lactose tetra-nitrate,  $C_{12}H_{18}(NO_2)_4O_{11}$ , separates out. It is a yellow powder containing no water (m. p. 80–81°); it begins to decompose at 90°, and is totally destroyed at 165°.

B. B.

**Glycogen.** By E. KÜLZ (*Ber.*, 15, 1300–1301).—In the course of some experiments on the elementary composition and specific rotatory power of glycogen from various sources, the author has found that glycogen, prepared according to Brücke's method, after being redissolved in water, is very imperfectly precipitated even on the addition



of large quantities of alcohol. A series of experiments showed that the degree of precipitation by alcohol is dependent on the degree of ash impurity of the preparation; the more impure the sample, the more complete is the precipitation. In the case of solutions in which no precipitation occurs, the addition of traces of sodium chloride renders it complete.

V. H. V.

**Carbohydrate in *Fucus Amylaceus* (continuation, *vide* p. 939).** By H. G. GREENISH (*Arch. Pharm.* [3], 20, 321—335).—The residue of the drug when treated with dilute hydrochloric acid, yields a solution from which an albumin-like precipitate is thrown down by alcohol. This precipitate obstinately retains mineral matters to the amount of 5·4 per cent. This substance ( $C_6H_{10}O_5$ ) is not identical with Reichardt's pararabin, and has been provisionally called paramylan. Paramylan is white, swelling in water to a transparent jelly, slightly soluble in water, from which it can be precipitated by basic lead acetate. Neutral lead acetate, copper sulphate, potash, hydrochloric acid, and lime water, do not affect its solutions. Fehling's solution is precipitated in blue flocks, but is not reduced. When paramylan is treated with sulphuric acid, it is converted into a sugar, whose specific rotatory power is  $[\alpha]_D = +61\cdot8^\circ$  (and  $64\cdot1^\circ$  by a second experiment). The dried sugar is yellow and very hygroscopic, soluble in water; it is precipitated by ammoniacal lead acetate, becoming red on boiling, and is fermentable. When further dried and dissolved in water, its rotatory power was diminished to  $[\alpha]_D = +47^\circ$ ; this index, which was less than that found in the first experiment, agrees closely with that for grape-sugar; the difference between the two experimental results is not explained. The reasons for considering this paramylan to be different from Reichardt's pararabin, are that pararabin is not directly convertible into sugar by boiling with acids, and when converted into metarabin and boiled with acid, it yields arabin. The residue above referred to was treated also with dilute and strong soda solution, and with potassium chlorate and nitric acid; the methods are fully detailed, as also the results; by the first solution metarabin was obtained, by the second a substance apparently identical with Thomsen's wood-gum, and by the last ordinary cellulose. Summing up the results of the whole paper, we find that the gelatinous substance in *Fucus amylaceus* is not identical with lichenin, as it is insoluble in ammoniacal copper solution, is not easily precipitated by alcohol, and is convertible by acids into sugar. It therefore appears to be identical with Payen's gelose. But the gelose is not pararabin, as the methods of separation and easy conversion into sugar indicate. No mannitol is found in the commercial article, but as the drug is moistened with water during its preparation, mannitol must be looked for in the fresh material. Extraction with dilute hydrochloric acid removes a saccharifiable carbohydrate, which produces grape-sugar, and is not pararabin. The cellulose present corresponds with that of the phanerogams.

Complete analysis of *Fucus amyl.*:—Moisture, 15·07; ash, 10·24; soluble in cold water (mucilage, &c.), 2·70; soluble in alcohol, 0·10; metarabin, 1·32; soluble in dilute NaHO, 3·12; paramylan, 6·52;

soluble in hot water (gelose), 36.71; wood-gum, 3.17; cellulose, 10.17; albuminoids, 7.48; other matters removable by potassium nitrate, loss, &c., 3.40; total, 100.00. E. W. P.

**Separation of Water within the Molecule.** By W. ROSE (Ber., 15, 1322—1323).—In this paper a comparison is drawn between

the anhydrides of typical formula,  $\begin{array}{c} \text{C}-\text{CO} \\ | \quad \diagup \\ \text{C}-\text{CO} \end{array} \text{O}$ , and lactones of formula

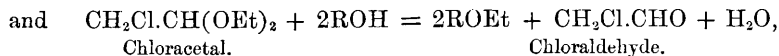
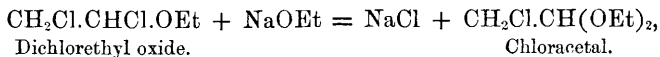
$\begin{array}{c} \text{C}-\text{CH}_2 \\ | \quad \diagup \\ \text{C}-\text{CO} \end{array} \text{O}$ ; the latter may be considered to be derived from the former by the replacement of one oxygen- by two hydrogen-atoms. Between the anhydrides and lactones there should exist a class of

substances, or hydroxylactones, of formula  $\begin{array}{c} \text{C}-\text{CH}(\text{OH}) \\ | \quad \diagup \\ \text{C}-\text{CO} \end{array} \text{O}$ , of which

Limpricht's half aldehyde of fumaric acid,  $\begin{array}{c} \text{CH}.\text{CH}(\text{OH}) \\ || \quad \diagup \\ \text{CH}.\text{CO} \end{array} \text{O}$ , is probably a member. V. H. V.

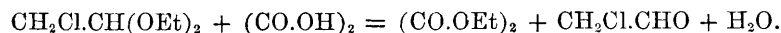
**Formation of Trimethylsulphine Iodide.** By H. KLINGER (Ber., 15, 881).—Trimethylsulphine iodide,  $\text{Me}_3\text{SI}$ , is formed together with other products, when a mixture of methyl iodide and arsenious sulphide is heated in sealed tubes at  $100^\circ$ . W. C. W.

**Monochloraldehyde.** By K. NATTERER (Monatsh. Chem., 3, 442—464).—This compound is prepared by the action of acids on monochloracetal, which is itself produced by the action of sodium ethylate on unsymmetrical dichlorethyl oxide:



R denoting an acid radicle.

The decomposition of the chloracetal may be effected by dilute sulphuric acid, normal butyric acid, or glacial acetic acid, less readily by acetic anhydride; but the best reagent for the purpose is dehydrated oxalic acid, the action of which on chloracetal may be represented by the equation—



The product is a *hydrate of chloraldehyde*,  $\text{CH}_2\text{Cl}.\text{CHO}.\frac{1}{3}\text{H}_2\text{O}$  or  $2(\text{CH}_2\text{Cl}.\text{CHO}).\text{H}_2\text{O}$ , which dissolves in water, alcohol, and ether, and separates from these solutions in monoclinic crystals, in which  $a:b:c = 1.2972:1:0.5442$  and angle  $ac = 95^\circ 14'$ . The crystals are tabular by predominance of the faces  $\infty P\infty$ , and the edge of the

tablets is bounded by the faces  $\infty P\infty$ ,  $+P\infty$  and  $+P$ . The dry crystals have a faint fruity smell; their vapour strongly attacks the mucous membrane; their solution produces yellow spots on the skin; and the aqueous solution reduces ammoniacal silver solution, with formation of a speculum. The hydrate has no definite melting point, but passes gradually (at  $43-50^\circ$ ) into the liquid state; it boils constantly (but only apparently without decomposition) at  $85.5^\circ$  (corr.), the distillate resolidifying completely. Vapour-density, obs. 1.984; calc. for  $2(\text{CH}_2\text{Cl}.\text{CHO}) + \text{H}_2\text{O} = 2.01$ . The vapour of the hydrate contains therefore the elements of 2 mols.  $\text{CH}_2\text{Cl}.\text{CHO}$  and 1 mol. water, a conclusion confirmed by the fact that when the vapour is passed over anhydrous calcium chloride at  $100^\circ$ , the calcium chloride takes up water and deliquesces, while anhydrous monochloraldehyde collects in the receiver in the form of a mobile pungent liquid. But whether this hydrate is actually composed of 2 mols.  $\text{C}_2\text{H}_3\text{ClO}$  and 1 mol. water, in which case it would belong to the class of so-called molecular compounds, or whether the component atoms are arranged in the manner represented by the formula  $\text{CH}_2\text{Cl}.\text{CH}(\text{OH}).\text{O}.\text{CH}(\text{OH}).\text{CH}_2\text{Cl}$ —in which case it would consist of ethyl oxide having two of its hydrogen-atoms symmetrically replaced by chlorine and two others by hydroxyl—is a question the decision of which must be left to further investigation.

The hydrate is not oxidised by exposure to the air, either moist or dry, but nitric acid oxidises it readily to monochloroacetic acid,  $\text{CH}_2\text{Cl}.\text{COOH}$ .

Monochloraldehyde, when kept in sealed glass tubes, is gradually converted into an amorphous porcelain-like mass consisting of a polymeric modification insoluble in water, alcohol, ether, and chloroform. When heated in open capillary tubes this polymeride does not melt, but gradually disappears from  $100^\circ$  upwards, while a liquid collects in the cold part of the tube, and resolidifies after a time to an amorphous mass. The density of the vapour thus produced is 2.77, which agrees very nearly with the calculated value for the formula  $\text{CH}_2\text{Cl}.\text{CHO}$ , showing that at  $100-200^\circ$  the amorphous polymeride is reconverted into monochloraldehyde.

When the crude product of the action of oxalic acid on chloroacetal (impure hydrate of monochloraldehyde) is cooled with ice and salt, and half its volume of cooled strong sulphuric acid is gradually added, with frequent agitation, the sulphuric acid at first dissolves, but soon afterwards a turbidity appears, and a thick oil separates, which after standing for some hours in a freezing mixture, solidifies to a compact crystalline mass; this when separated from the lower layer, consisting chiefly of sulphuric acid, and purified by washing, first with ice-cold water, then with cold alcohol, and crystallisation from hot alcohol, exhibits the composition of monochloraldehyde, and is in fact a crystallised polymeride of that compound. It is insoluble in water, slightly soluble in cold alcohol, easily in hot alcohol and in ether. The crystals are rhombic, having the axes

$$a : b : c = 1.5003 : 1 : 0.9407,$$

needle-shaped by predominance of the faces  $P\infty$  and  $\infty P\infty$ , and

bevelled by  $P\infty$ , P and  $P\frac{1}{2}$ . They melt at  $87-87.5^{\circ}$  (corr.) and are reconverted into monochloraldehyde by distillation; and this transformation affords the best means of obtaining liquid monochloraldehyde in the pure state.

H. W.

**Action of Hydroxylamine on Acetone.** By V. MEYER and A. JANNY (*Ber.*, 15, 1324—1326).—In order to throw light on the constitution of nitrosoacetone and the products of the action of hydroxylamine on substituted acetones, the authors have examined the action of hydroxylamine on acetone itself. By this reaction a compound is formed, which, on account of its relation to acetoximic acid, the authors name *acetoxime*, thus:  $Me.CO.Me + NH_3O = H_2O + Me_2CNHO$ ; it crystallises in colourless transparent prisms (m. p.  $60^{\circ}$ , b. p.  $134.8^{\circ}$ ) soluble in water, alcohol, ether, &c.; it has a neutral reaction, and is very volatile, emitting an odour resembling that of chloral. In order to throw light on its constitution, the authors intend to examine the action of hydroxylamine on other ketones and aldehydes, and have found, in the course of preliminary experiments, that ethaldehyde and chloral form crystalline nitrogenous products. Of the two formulæ for acetoximic acid,  $Me.CO.CN_2H_3O$  and  $Me.CHNO.CHHNO$ , the authors incline to the second, on account of the readiness with which hydroxylamine reacts with the oxygen-atom of the acetone; and inasmuch as acetoximic acid is formed by the action of hydroxylamine both on nitroso- and on dichlor-acetone, the nitrogenous group of acetoximic acid must be identical with that of nitrosoacetone, so that the problem of determining the constitution of nitrosoacetone rests upon the determination of the constitution of acetoximic acid.

V. H. V.

**Chlorotribromopropionic Acid.** By C. F. MABERY and H. C. WEBER (*Amer. Chem. J.*, 4, 104—106).—This acid is best prepared by heating chlorobromacrylic acid with a slight excess of bromine at  $100^{\circ}$  for two hours in a closed tube, then removing the excess of bromine by spontaneous evaporation, and purifying the product by pressure between filter-paper and crystallisation from carbon bisulphide. It dissolves readily in ether and alcohol, less readily in cold than in hot carbon bisulphide, and chloroform. In contact with water it forms an oil which does not solidify at  $0^{\circ}$ . From carbon bisulphide or chloroform it crystallises by slow evaporation in triclinic prisms melting at  $102-103^{\circ}$ . The *barium salt*,  $(C_3HClBrO_2)Ba$ , crystallises in slender oblique prisms soluble in cold water; the *calcium salt* in clusters of needles; the *potassium salt*,  $C_3HClBrO_2K.H_2O$ , in rhombic prisms freely soluble in cold water; the *silver salt* is very unstable; the *barium salt* is comparatively stable, but decomposes slowly when heated in aqueous solution, apparently yielding tribromacrylic acid.

*Chlorobromacrylic acid*,  $C_3H_2ClBrO_2$ , also takes up hydrogen bromide, forming an addition-product, probably chlorodibromopropionic acid, which melts at  $80^{\circ}$ .

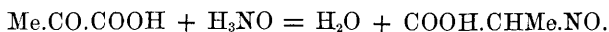
H. W.

**A New Method of Preparing  $\alpha$ -Nitrosopropionic Acid and the Mode of Action of Hydroxylamine.** By V. MEYER and A. JANNY (*Ber.*, 15, 1525—1529).—The action of hydroxylamine

on the acetones and aldehydes of the fatty series, has been shown by the authors to consist essentially in the conversion of the CO-group into CNOH. As a step towards the solution of the constitution of the CNOH-group in the products in question, of which the following are

the possible expressions  $\text{=C:N.OH}$   $\text{=C} \begin{smallmatrix} \text{NH} \\ \diagup \\ | \\ \text{O} \end{smallmatrix}$   $\text{=C} \begin{smallmatrix} \text{H} \\ \diagup \\ \text{NO} \end{smallmatrix}$ , and

which will be elucidated by the study of the products themselves, now in progress, the authors have attacked the more general question as to whether a true nitroso-body can be formed by the hydroxylamine reaction. By the action of this base on pyroracemic acid they have succeeded in obtaining  $\alpha$ -nitrosopropionic acid according to the equation:



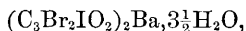
The reaction proceeds so smoothly and may be carried out with such small quantities of substance, that it may be used as a test for the presence of pyroracemic acid.

Since  $\alpha$ -nitrosopropionic acid is an undoubtedly normal nitroso-body, being converted, *i.e.*, by nascent hydrogen, into the amido-compound, it would seem to be established that hydroxylamine reacts with the CO-group to form a true nitroso-group. In face, however, of the variable nature of the reaction with the ketones, the authors hesitate to generalise thus far. Moreover the energetic character of the reaction of acetoxime with acetic chloride and anhydride, the fact of nitrosopropionic acid remaining in contact with this latter reagent inert, argues in this case for an oximid- rather than a nitroso-formula.

For the further elucidation of these problems, the authors are studying the action of hydroxylamine on aldehyde and ethylene oxide. They remark, in conclusion, that Liebermann's reaction is inapplicable to the diagnosis of the fatty nitroso-compounds, owing to the wide variations in the results which it gives. The nitrosamines appear, however, to be an exception, giving the characteristic reaction brilliantly.

C. F. C.

**Dibromiodacrylic and Chlorobromiodacrylic Acids.** By C. F. MABERY and RACHEL LLOYD (*Amer. Chem. J.*, **4**, 92—100).—*Dibromiodacrylic acid*,  $\text{C}_3\text{HBr}_2\text{IO}_2$ , formed by direct addition of iodine monobromide to bromopropiolic acid,  $\text{C}_3\text{HBrO}_2$  (*Abstr.*, 1879, 225, 610), dissolves readily in ether, alcohol, carbon bisulphide, and chloroform, rather sparingly in cold water, and separates from a hot concentrated aqueous solution, at first as an oil, which crystallises on cooling in monoclinic prisms. It melts at  $139\text{--}140^\circ$  and sublimes slowly at higher temperatures. The solution saturated at  $20^\circ$  contains 1.4 p.c. of the crystallised acid. The *barium salt*,



prepared by neutralisation, is very soluble in hot, less so in cold water, and crystallises in rhombic prisms which give off their crystal-water at  $80^\circ$ . The *calcium salt*,  $(\text{C}_3\text{Br}_2\text{IO}_2)_2\text{Ca}$ , separates from concentrated solution in clusters of anhydrous needles less soluble in hot than in

cold water. The *potassium salt*,  $C_3Br_2IO_2K(?)$ , forms rhombic, highly deliquescent plates. The *silver salt*,  $C_3Br_2IO_2Ag$ , is precipitated by silver nitrate from the hot aqueous solution of the acid, in hexagonal plates which are slightly altered by exposure to light.

Dibromiodacrylic acid heated with bromine at  $100^\circ$  in a sealed tube is converted into tribromacrylic acid,  $C_3HBr_3O_2$ , melting at  $115-118^\circ$ .

*Chlorobromiodacrylic acid*,  $C_3HClBrIO_2$ , prepared by heating bromopropiolic acid with iodine monochloride dissolved in ether, is readily soluble in ether and in alcohol, somewhat less in carbon bisulphide and chloroform, and separates from a hot solution on cooling in monoclinic prisms, isomorphous with those of dibromiodacrylic acid. When slowly crystallised by evaporation of its solution in carbon bisulphide, it melts at  $115-116^\circ$ . It sublimes freely at somewhat higher temperatures. Its *barium salt*,  $(C_3ClBrIO_2)_2Ba, 3\frac{1}{2}H_2O$ , is soluble in cold, more freely in hot water, and separates on cooling in rectangular prisms, which give off all their water on mere exposure to the air.  $(C_3ClBrIO_2)_2Ca, H_2O$  crystallises in branching needles which give off their water at  $80^\circ$ .  $C_3ClBrIO_2K?$  is very deliquescent.  $C_3ClBrIO_2Ag$  forms rhombic prisms, sparingly soluble in cold, more freely in hot water.

H. W.

**Synthesis of Oxalic Acid.** By V. MERZ and W. WEITH (*Ber.*, 15, 1507—1513).—The authors have investigated the conversion, under varying conditions, of the formates of the alkalis and alkaline earths into oxalates. Sodium formate, when heated over a naked flame, melts at first to a limpid liquid, which, on continuing to raise the temperature, froths considerably, from evolution of hydrogen, becoming viscous, and ultimately solidifying to a crystalline mass. If the liquid is continually stirred, a homogeneous mass is obtained, which, in one experiment, the authors found to contain:  $Na_2C_2O_4$ , 50.4 per cent.;  $Na_2CO_3$ , 13 per cent. On the other hand, if the heating is unaccompanied by stirring, the product contains two layers; the upper white, the lower dark-coloured. The mean percentage of the salts in this case was found in one experiment to be  $Na_2C_2O_4$ , 21 per cent.;  $Na_2CO_3$ , 14.5 per cent.

The subsequent experiments were conducted in a glass tube, 15—20 mm. in diameter, terminating in a bulb at its lower end, and contained within a second tube of 45—50 mm. diameter, partly filled with a liquid, which could be heated to the temperature required, and served as the bath for heating the former. The liquids used were diphenylamine, mercury, and sulphur. The results of the experiments were as follows:—

*Sodium Formate.*

No.	Temp.	Duration.	Atmosphere.	Product contained.	
				$\text{Na}_2\text{C}_2\text{O}_4$ per cent.	$\text{Na}_2\text{CO}_3$ per cent.
1	310°	5 hrs.	Air	0	traces
2	360	"	"	20·8	56·5
3	"	"	Partial vacuum	27·9	54·4
4	"	"	CO <sub>2</sub>	7·1	50·9
5	420	50 min.	Partial vacuum	54·4	37·8
6	"	"	"	52·7	—
7	"	"	"	71·6	28·7
8	"	"	"	72·1	28·1
9	"	1 hr.	Air	37·8	59·5
10	"	"	Stream of air	29·6	—
11	"	"	Partial vacuum	52·8	—
12	"	"	"	75·2	—
13	"	"	Hydrogen	54·6	—
14	"	"	CO <sub>2</sub>	29·5	59·2

The conditions most favourable to the formation of oxalate are a partial atmosphere of air, and a rapid application of heat.

*Potassium Formate.*

No.	Temp.	Duration.	Atmosphere.	Product contained.	
				$\text{Na}_2\text{C}_2\text{O}_4$ per cent.	$\text{Na}_2\text{CO}_3$ per cent.
1	360°	5 hrs.	Air	0	41·3
2	"	10 "	"	0	93·3
3	"	5 "	Partial vacuum	0	35·1
4	420	1 hr.	Air	43·0	56·6
5	"	1 "	Partial vacuum	66·7	31·8
6	"	1 "	CO <sub>2</sub>	20·7	—

*Rubidium formate* at 360° is decomposed in a similar manner, but more slowly than the potassium salt, carbonate being formed, but no oxalate.

*Calcium formate* is only slowly decomposed at 360°. After heating for five hours in one experiment, the mass was found to contain 5 per cent.  $\text{CaCO}_3$ , but no oxalate. In the sulphur bath (440°) the decomposition was more rapid. At the expiration of one hour, in one experiment, the mass was found to contain 54·5 per cent.  $\text{CaCO}_3$ , 0·5 per cent. of a carbonaceous residue, but no oxalate.

*Barium formate* was decomposed gradually at 360°. After the expiration of five hours, the resulting mass contained 85 per cent.  $\text{BaCO}_3$ . In a partial vacuum, at the same temperature, the percentage of carbonate formed in the same time was 39. No oxalate was formed either at this temperature or at 440°.

*Magnesium formate* is decomposed slowly at 360°, but without formation of oxalate. After five hours' heating in one experiment, the mass contained 16·1 per cent. carbonate.

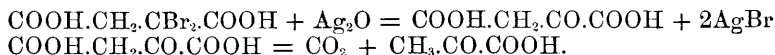
*Conversion of Oxalates into Carbonates.*—The alkaline oxalates were

found to be only slightly decomposed at the temperature of the sulphur bath. After five hours' heating, the mass contained, in the case of the sodium salt, 5 per cent.  $\text{Na}_2\text{CO}_3$ ; in the case of the potassium salt, 3.95 per cent.  $\text{K}_2\text{CO}_3$ .

The gas evolved during the decomposition of the oxalate is not pure carbonic oxide, but a mixture of carbonic anhydride and monoxide. According to the author's experiments upon dipotassic oxalate, perfectly dehydrated and heated in an atmosphere of nitrogen, the ratio (volumes) varies from 1 : 11 to 1 : 14.5.

Sodium formate, heated at  $420^\circ$ , is largely converted into oxalate, the yield amounting to 70—75 per cent. of the resulting mass. Moreover, the synthesis of the formate from carbon monoxide and sodium hydroxide, *i.e.*, soda-lime, offers no difficulties; and the separation of the disodic oxalate formed, from the formate, is easily effected by recrystallisation from hot water. The yield of oxalic acid in the ordinary process of fusing sawdust with a mixture of sodium and potassium hydroxide, does not exceed 50 per cent. of the weight of the latter. The yield from the formate, calculated from the composition of the product, *i.e.*, containing 60—70 per cent. oxalate, is much higher, with the additional advantages of involving the exclusive use of the cheaper alkali, and furnishing a product of a high degree of purity. The authors leave it to the technologists to decide as to the employment of the process on the large scale. C. F. C.

**Isodibromosuccinic Acid.** By F. BEILSTEIN and E. WIEGAND (*Ber.*, 15, 1499—1500).—The debromination of this acid by means of silver oxide was found to occur according to the equations:—



The acid formed in this way behaved like pyroracemic acid.

C. F. C.

**Certain New Tartrantimonites.** By F. W. CLARKE (*Ber.*, 15, 1540).—It has been previously shown that tartar emetic is the potassium salt of a peculiar complex acid, which is monobasic, and to which the term tartrantimonious may be applied. The following salts of this acid have been prepared by double decomposition of its barium salt with the sulphates of the respective bases.

The aniline salt,  $\text{SbC}_4\text{H}_5\text{O}_7.\text{C}_6\text{H}_7\text{N}$ , crystallises in long white prisms, sp. gr. 1.890 at  $11^\circ$ . The salts of quinine and atropine were obtained as gummy masses, the former anhydrous, the latter containing 2 mols.  $\text{H}_2\text{O}$ . C. F. C.

**Action of Sodium Thiosulphate on Ketonic Acids.** By C. BÖTTINGER (*Ber.*, 15, 892).—When molecular proportions of sodium thiosulphate and pyroracemic acid are ground to a paste with water, sulphur is liberated. The aqueous solution of the crude product deposits crystals which are insoluble in alcohol. Their composition may probably be represented by the formula  $\text{SO}_3\text{Na}.\text{CMe}(\text{HO}).\text{COONa}$ .

W. C. W.



**Nitrosacetone and Acetoacetic Acid.** By M. CERESOLE (*Ber.*, 15, 1326—1328).—Experiments in V. Meyer's laboratory have shown that on heating ethylic acetoacetate with aqueous alkalis and nitrous acid, it yields both nitrosacetone and ethylic nitrosacetoacetate. The author has more minutely examined the condition of this reaction, in order to discover the intermediate factor which leads to the formation of nitrosacetone on the one hand, and to ethylic nitrosacetoacetate on the other; and finds that a freshly-prepared solution of ethylic acetoacetate in alkali yields the nitroso-derivative, while a similar solution kept for twenty-four hours gives nitrosacetone. This latter solution contains the potassium salt of an acid, whose properties and composition of barium salt agree with those of the non-isolated acetoacetic acid,  $\text{Me.CO.CH}_2\text{COOH}$ . In order to obtain the barium salt, the alkaline solution of ethylic acetoacetate is allowed to stand for twenty-four hours, then acidified with sulphuric acid, shaken up with ether, and the extract is carefully distilled. The mixture of the acid and unchanged ethylic acetoacetate is rubbed up with barium carbonate, and the barium salt extracted with ether. It is an amorphous salt, soluble in water, and giving with ferric chloride a violet-red coloration. The free acid is a thick, colourless syrup, giving a strongly acid solution, and decomposing violently at  $100^\circ$ , with evolution of carbonic anhydride and acetone; with nitrous acid, it gives directly carbonic anhydride and nitrosacetone. This new acid is probably identical with the substance giving a reddish coloration with ferric chloride, which Tollens found in diabetic urine (*Abstr.*, 1881, 1162).  
V. H. V.

**Action of Bromine in Alkaline Solutions on Amides.** By A. W. HOFMANN (*Ber.*, 15, 752—762, and 762—775). Parts III and IV.

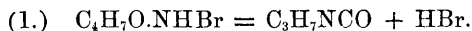
III. It has been already shown that acetamide, when treated with bromine and sodium hydroxide, yields a bromo-derivative, and under other conditions a substituted carbamide, viz., methylacetyl carbamide (this vol., 822, and *Ber.*, 15, 407). In the case of the lower homologues of acetamide, similar compounds are formed; but with the homologues containing more than four atoms of carbon, the bromo-derivatives are not easily obtained, the products in all cases consisting of the substituted carbamides.

*Formamide* yields a monobromoformamide,  $(\text{CHO})\text{NHBr}$ , which has not been isolated, but is further resolved into hydrobromic acid and cyanic acid, the latter being converted by polymerisation into cyanuric acid.

From *propionamide* the compound  $(\text{C}_3\text{H}_5\text{O})\text{NHBr}$  has been obtained. It is more soluble than the corresponding acetyl-compound, and crystallises in flat colourless needles, melting at  $80^\circ$ . By alkalis it is resolved into hydrobromic acid, carbonic anhydride, and ethylamine. *Ethyl-propionyl carbamide*,  $\text{NHEt.CO.NH}(\text{C}_3\text{H}_5\text{O})$  is prepared from propionamide; it crystallises in slender needles, melting at  $100^\circ$ . It is decomposed by nitric acid, yielding propionic acid and nitrate of monethylcarbamide.

*Isobutyramide* yields a monobromo-derivative,  $(\text{C}_4\text{H}_7\text{O})\text{NHBr}$ , crys-

tallising from water in colourless transparent needles melting at  $92^{\circ}$ ; caustic alkalis convert this compound into hydrobromic acid, carbonic anhydride, and isopropylamine. The reaction takes place in two stages, and when sodium carbonate is used, the decomposition reaches only the first stage, and isopropyl cyanate is formed. The following equations represent this decomposition :—



*Isopropyl-isobutyryl carbamide*,  $\text{NHC}_3\text{H}_7\text{.CO.NH(C}_4\text{H}_7\text{O)}$ , crystallises from alcohol in tablets melting at  $86^{\circ}$ . Its formation is accompanied by that of di-isopropyl carbamide,  $\text{CO(NHC}_3\text{H}_7)_2$ .

Normal butyramide is the first of the amides, which do not form bromo-derivatives, which can be isolated. Like the higher amides, it is easily converted into a carbamide, viz., propyl-butyryl carbamide,  $\text{NHC}_3\text{H}_7\text{.CO.N.HC}_4\text{H}_7\text{O}$ , which crystallises in colourless leaflets, sparingly soluble in water, easily soluble in alcohol and ether, melting at  $99^{\circ}$ .

*Isobutylvaleryl carbamide*,  $\text{NHC}_4\text{H}_9\text{.CO.N.H(C}_5\text{H}_9\text{O)}$ , obtained from valeramide, crystallises in colourless lustrous needles, melting at  $102^{\circ}$ .

*Amylcaproyl carbamide*,  $\text{NHC}_5\text{H}_{11}\text{.CO.NH(C}_6\text{H}_{11}\text{O)}$ , obtained from the amide of normal caproic acid, forms colourless leaflets (m. p.  $97^{\circ}$ ). *Amylisocaproyl carbamide* is obtained from the amide of isocaproic acid (isobutylic acid); it melts at  $94^{\circ}$ .

In the seven-carbon series oenanthylamide was used, and found to yield *hexyloenanthyl carbamide*,  $\text{NHC}_6\text{H}_{13}\text{.CO.NH(C}_7\text{H}_{13}\text{O)}$ . It forms lustrous leaflets, melting at  $97^{\circ}$ , is insoluble in water, and less soluble in alcohol than its lower homologue.

In the next series *octoxyamide* was taken. This amide is prepared from the caprylic acid obtained by oxidising the higher-boiling portions of fusel oil. It forms *heptyloctoxyl carbamide*,  $\text{NHC}_7\text{H}_{15}\text{.CO.NH(C}_8\text{H}_{15}\text{O)}$ , which crystallises in small leaflets (m. p.  $86^{\circ}$ ).

*Octylnonoxyl carbamide*,  $\text{NHC}_8\text{H}_{17}\text{.CO.NH(C}_9\text{H}_{17}\text{O)}$  (m. p.  $87^{\circ}$ ), is obtained from the amide of nonoic acid, prepared by Krafft and Becker by the oxidation of castor-oil.

*Nonyldecoxyl carbamide*,  $\text{NHC}_9\text{H}_{19}\text{.CO.NH(C}_{10}\text{H}_{19}\text{O)}$ , forms white lustrous leaflets (m. p.  $101^{\circ}$ ). It is obtained from the amide of capric acid, which, like caprylic acid, is obtained by oxidising fusel oil.

*Stearamide* has also been subjected to the action of bromine and caustic potash, and is found to yield *heptadecylstearyl carbamide*,  $\text{NHC}_{17}\text{H}_{35}\text{.CO.NH(C}_{18}\text{H}_{35}\text{O)}$ , which crystallises in leaflets having a mother-of-pearl lustre (m. p.  $112^{\circ}$ ).

IV. This portion of the investigation is concerned with the formation of the primary amines by the action of caustic alkalis on the product obtained by treating amides with bromine. In this way acetamide yields methylamine, free from the secondary or tertiary amine, and the yield is such, viz., 87 per cent. of the theoretical, that the amide may be used as a method of preparing methylamine. To this end a mixture of 1 mol. acetamide and 1 mol. bromine is treated

with a cold solution of caustic potash (10 per cent. KHO) until it becomes yellow. The product so obtained is heated at 60—70° with a further quantity of caustic potash (3 mols. KHO to 1 mol. acetamide). In 10 or 15 minutes the solution is decolorised, and contains no longer bromacetamide, but methylamine, which latter is driven off by the application of heat, and collected in hydrochloric acid. The crude chloride contains some ammonium chloride, which is easily separated by crystallisation from absolute alcohol. Some other compounds are formed simultaneously, amongst which may be mentioned carbon tetrabromide, and a compound having the formula  $\text{MeNBr}_2$ , which is also produced when methylamine hydrochloride is treated with bromine.

In a similar manner, ethylamine is obtained from propionamide, isopropylamine from isobutyramide, and propylamine from butyramide. Isobutylamine (b. p. 65—67°) was prepared from valeramide. Normal pentylamine,  $\text{CH}_3(\text{CH}_2)_4\text{NH}_2$ , is obtained from normal capronamide; it is a liquid boiling at 103°, a boiling point which is higher than that of any of the isomerides. Isocapronamide yields an amylamine (isobutylmethylamine), boiling at 95—96°, and identical with that described by Wurtz (*Ann. Chim. Phys.*, **30**, 44).

Normal hexylamine,  $\text{CH}_3(\text{CH}_2)_5\text{NH}_2$ , is obtained from the amide of oenanthylic acid; it is identical with that described by Pelouze and Cahours (*Annalen*, **124**, 295).

Heptylamine is obtained from octoxylamide. It is a liquid boiling at 153—155°; consequently much higher than that obtained by Pelouze and Cahours (*Ann. Chim. Phys.* [4], **1**, 5, and Schorlemmer (this Journal, **16**, 221), from the heptane found in petroleum.

Octylamine is best prepared by digesting octylnonoxyl carbamide with concentrated hydrochloric acid; it boils at 171—174°.

Nonylamine is obtained from decoxylamide (capramide); it boils at 195°.

Heptadecylamine is obtained by fusing heptadecylstearyl carbamide with caustic potash, or by heating this compound with hydrochloric acid at 200°. In this latter case, the product of the reaction consists of heptadecylamine hydrochloride, stearamide, and stearic acid, from the alcoholic solution of which platinum chloride precipitates the platino-chloride of heptadecylamine in yellow leaflets, from which the base has been prepared. It is a solid fat-like substance, inodorous, non-volatile in steam, but may be distilled without decomposition, is insoluble in water, but soluble in alcohol, forming an alkaline solution. Its hydrochloride is insoluble in water, but soluble in alcohol. P. P. B.

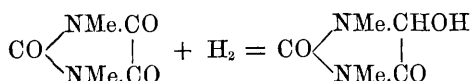
**Dimethyl-glyoxyl-carbamide, a Reduction-product of Cholestrophane.** By R. ANDREASCH (*Monatsh. Chem.*, **3**, 436—441).—Limpricht, by reducing parabanic acid or oxalylcarbamide,



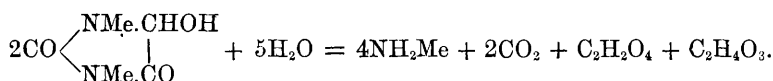
with zinc and hydrochloric acid, obtained the compound of the parabanic series analogous to alloxantin, viz., oxalantin,  $\text{C}_6\text{H}_4\text{N}_4\text{O}_5$ , according to the equation  $2\text{C}_3\text{H}_2\text{N}_2\text{O}_3 + \text{H}_2 = \text{H}_2\text{O} + \text{C}_6\text{H}_4\text{N}_4\text{O}_5$ .

Dimethyl-parabanic acid or cholestrophane,  $\text{CO}(\text{NMe}.\text{CO})_2$ , how-

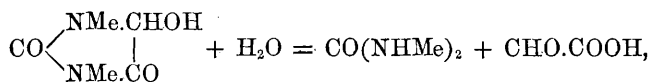
ever, reacts with zinc and hydrochloric acid in a totally different manner, the product consisting of dimethylglyoxyliccarbamide,  $C_5H_8N_2O_3$ , formed according to the equation—



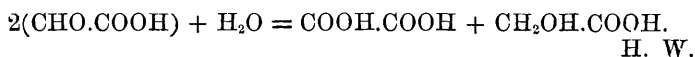
Dimethylglyoxyliccarbamide is crystalline, and melts below  $100^\circ$  to a colourless liquid, which at a higher temperature volatilises without decomposition, forming a sublimate of oily drops on the cooler part of the tube. By oxidising agents, chromic mixture for example, it is reconverted into cholestrophane. By boiling in moderately dilute solution with excess of barium hydroxide, it is resolved into carbonic, oxalic, and glycollic acids and methylamine, as shown by the equation,



The reaction, however, takes place by two stages, the first consisting in the formation of dimethylcarbamide and glyoxylic acid—



the second in the conversion of the dimethylcarbamide into methylamine and carbonic anhydride:  $CO(NHMe)_2 + H_2O = 2NH_2Me + CO_2$ ; and of the glyoxylic acid into oxalic and glycollic acids:



H. W.

**Methyl-alloxantins.** By R. ANDREASCH (*Monatsh. Chem.*, **3**, 428—432).—*Dimethyl-alloxantin*,  $C_8H_4(CH_3)_2N_4O_8$ , admits of two modifications, represented by the following formulæ:—



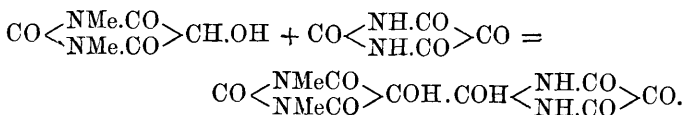
Symmetrical.



Unsymmetrical.

The first, which has its two methyl-groups in different alloxan-residues, is formed, as already mentioned (p. 633), by the action of hydrogen sulphide on the product obtained by treating theobromine with potassium chlorate and hydrochloric acid, which contains monomethylalloxan: consequently the two methyl-groups in the product must be situated one in each alloxan-group of the alloxantin molecule; in other words, its structure must be symmetrical.

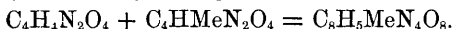
The unsymmetrical modification is formed by the action of alloxan on dimethyldialuric acid:



A solution of dimethyldialuric acid, obtained by reduction of dimethylalloxan with hydrogen sulphide at the boiling heat, is mixed with a solution of alloxan in a small quantity of water, whereupon the dimethylalloxantin is deposited in the form of a crystalline powder. It may be purified by crystallisation from a small quantity of hot water, and then forms microscopic, four-sided, very acute pyramids usually grouped in stellate druses. It is insoluble in alcohol and in ether, and is decomposed by heat, with formation of a violet-coloured deposit.

Unsymmetrical dimethylalloxantin might also be expected to result from the union of dialuric acid with dimethylalloxan, but an experiment made with this view, an excess of the latter being employed, yielded not di-, but tetra-methylalloxantin (amalic acid).

*Monomethylalloxantin*,  $\text{C}_9\text{H}_8\text{N}_4\text{O}_8$ , is formed on mixing the aqueous solutions of dialuric acid and monomethylalloxan, and separates as a crystalline precipitate, convertible by recrystallisation from a small quantity of warm water into druses of thin microscopic tablets with rhomboidal outline, having the composition  $\text{C}_9\text{H}_8\text{N}_4\text{O}_8, 3\text{H}_2\text{O}$ . Its formation is represented by the equation,



H. W.

**Cyamidamalic Acid.** By R. ANDREASCH (*Monatsh. Chem.*, **3**, 433—435).—E. Mulder, by treating alloxantin with cyanamide, obtained isouric acid and alloxan, according to the equation  $\text{C}_8\text{H}_6\text{N}_4\text{O}_8 + \text{CN}_2\text{H}_2 = \text{C}_5\text{H}_4\text{N}_4\text{O}_3 + \text{C}_4\text{H}_4\text{N}_2\text{O}_5$  (this Journal, 1874, 255). The author therefore expected that a similar treatment of tetramethylalloxantin (amalic acid) would yield dimethylisouric acid. Experiment showed, however, that the reaction takes place in a different way, leading to the production of cyamidamalic acid,  $\text{C}_{13}\text{H}_{14}\text{N}_6\text{O}_2$ , according to the equation  $\text{C}_8\text{H}_2(\text{CH}_3)_4\text{N}_4\text{O}_3 + \text{CN}_2\text{H}_2 = \text{C}_{13}\text{H}_{14}\text{N}_6\text{O}_2 + \text{H}_2\text{O}$ . When 4 g. amalic acid and 2 g. cyanamide are boiled in about 100 c.c. water, the whole gradually dissolves, and the solution on cooling deposits a crystalline powder of cyamidamalic acid, which, when purified by recrystallisation from hot water, forms short highly lustrous needles. It is soluble in alcohol and ether, sparingly in cold, somewhat freely in boiling water. Its melting point cannot be determined, as it decomposes when heated, giving off purple-red vapours, and yielding a sublimate of the same colour; it turns perceptibly red also, even during drying at  $90^\circ$  or  $100^\circ$ .

Cyamidamalic acid is slowly dissolved by ammonia, without coloration, the solution reducing silver nitrate when heated therewith. It dissolves much more readily in caustic potash or soda, and the solution reduces silver even in the cold, more quickly and completely

when heated; also in mineral acids even at ordinary temperatures, forming neutral solutions. H. W.

**Derivatives of  $\alpha$ -Dinitrochlorobenzene.** By H. LEYMAN (Ber., 15, 1233—1237).—The author has studied the action of various amines on  $\alpha$ -dinitrochlorobenzene.

Trimethylamine gives with  $\alpha$ -dinitrochlorobenzene dinitrodimethylaniline (identical with that obtained by the direct nitration of dimethylaniline), according to the reaction  $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{Cl} + \text{NMe}_3 = \text{C}_6\text{H}_3(\text{NO}_2)_2\text{NMe}_2 + \text{MeCl}$ . A similar reaction takes place between paranitrochlorobenzene and trimethylamine. By digesting dinitrodimethylaniline with 2 mols. bromine, a methyl group is removed, and on further treatment with bromine, dinitraniline is formed, which is converted by excess of the bromine into bromonitraniline.

By the action of dimethylaniline on  $\alpha$ -dinitrochlorobenzene, dinitromethyldiphenylamine,  $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{NMePh}$ , is formed; it crystallises in golden glistening scales (m. p.  $167^\circ$ ).

Monomethylaniline and  $\alpha$ -dinitrochlorobenzene give dinitromethylaniline (m. p.  $167^\circ$ ); on substituting orthotoluidine an isomeric body (m. p.  $101^\circ$ ) is obtained.

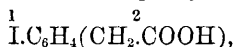
By the action of bromine on dinitromethyldiphenylamine, a monobromo-derivative is formed crystallising in four-sided tables (m. p.  $194^\circ$ ).

With  $\alpha$ -dinitrochlorobenzene, tolylenediamine gives a dinitrophenyltoluenediamine,  $\text{C}_6\text{H}_3(\text{NO}_2)_4\text{NH}\text{C}_7\text{H}_6\text{NH}_2$ , which crystallises in red tables (m. p.  $184^\circ$ ); it gives a formyl (m. p.  $157^\circ$ ) and an acetyl derivative (m. p.  $163^\circ$ ).

Metaphenylenediamine and  $\alpha$ -dinitrochlorobenzene form dinitrophenyl phenylenediamine,  $\text{NH}_2\text{C}_6\text{H}_4\text{NH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2$ , which melts at  $172^\circ$ . The author is engaged in further researches. V. H. V.

**Orthiodobenzyl Bromide and its Derivatives (Preliminary Notice).** By C. F. MABERY and F. C. ROBINSON (Amer. Chem. J., 4, 101—103).—This compound is formed by the action of bromine on orthiodotoluene at temperatures near the boiling point of the latter. It dissolves readily in ether, hot alcohol, benzene, carbon bisulphide, and chloroform, but is nearly, if not quite, insoluble in water, and very sparingly soluble in cold petroleum, from which it crystallises in flattened prisms often 2 or 3 cm. long. From a hot solution it separates in short thick prisms. It appears to be more volatile than the corresponding *para*-compound, and its vapour affects the mucous membrane in the same manner as the vapours of all other benzyl-compounds hitherto examined. It melts at  $52$ — $53^\circ$ , and sublimes slowly at higher temperatures in oily drops, which solidify in radiating needles. By oxidation with dilute nitric acid, it is converted into *o*-iodobenzoic acid melting at  $150$ — $155^\circ$ , identical with that obtained by Kekulé from orthiodotoluene (this Journal, 1875, p. 64).

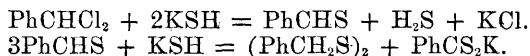
The constitution of the *o*-iodobenzyl bromide was further established by converting it, in the usual way, first into the corresponding nitril, and then into *o*-iod- $\alpha$ -toluic or *o*-iodophenylacetic acid,



which, as thus prepared, crystallises in felted groups of slender needles (m. p. 95—96°). The quantity obtained was, however, not sufficient for a satisfactory determination of the melting point, which the authors think is probably somewhat higher. This point, together with others relating to the acid, is therefore reserved for further investigation. The *primary amine* formed by treating the bromide with alcoholic ammonia yielded a platinochloride,  $(C_7H_6INH_3)_2PtCl_6$ , crystallising in pale yellow microscopic prisms, sparingly soluble in water and in cold alcohol, readily in hot alcohol, insoluble in ether.

H. W.

**Sulphobenzene.** By H. KLINGER (*Ber.*, 15, 861—865).—The author proves that the "sulphobenzene" which Fleischer (*Annalen*, 140, 234) obtained by the action of excess of potassium sulphhydrate on benzal chloride, is in reality benzyl bisulphide. The reaction takes place in two stages, benzothialdehyde being formed, which afterwards splits up into benzyl bisulphide and dithiobenzoic acid.



Alcoholic potassium sulphhydrate easily converts  $\alpha$ -benzothialdehyde into benzyl bisulphide and dithiobenzoic acid, but does not attack  $\beta$ -benzothialdehyde.

When two molecules of potassium sulphhydrate act on one molecule of benzal chloride in aqueous or alcoholic solution, the chief products of the reaction are benzyl bisulphide and benzothialdehyde sulphhydrate,  $2PhCHS, H_2S$ , while sulphuretted hydrogen, dithiobenzoic acid, and potassium chloride are also formed.

The  $\beta$ -thiobenzoic acid which Fleischer prepared by the oxidation of "sulphobenzene" is probably a mixture of benzoic and benzylsulphonic acids.

W. C. W.

**Laws of Substitution of Aromatic Amines.** By C. LANGER (*Ber.*, 15, 1328—1333).—In a former communication the author has shown that ortho- and para- mono- and di-substituted anilines take up that number of halogen-atoms which is required for the formation of trisubstituted anilines; but in the case of the meta-derivatives, the substituted groupings have no influence on the further substitution. In the present paper, these generalisations are further examined by a study of the substitution of symmetrical meta-substituted amines. By the action of bromine on metadibromaniline, Körner obtained pentabromaniline, by the action of chlorine on the same compound, he obtained a mixture of trichlorodibromaniline and tetrachloromonobromaniline, the latter being formed by the replacement of a bromine- by a chlorine-atom; it crystallises in white needles (m. p. 227), sparingly soluble in alcohol, ether, &c. By the action of amyl nitrite on trichlorodibromaniline, trichlorodibromobenzene is formed, crystallising in delicate needles (m. p. 149°), soluble in alcohol.

Similarly the author studied the action of halogens on symmetrical dichloraniline; and by the action of chlorine obtained pentachloraniline, which crystallises in large white needles (m. p. 235°), soluble in

ether and alcohol. By the further action of chlorine on pentachloroaniline, a compound crystallising in golden pyramids was formed, which contained no nitrogen, and probably had the formula  $C_6Cl_6O$ , being analogous to the pentabromophenol bromide,  $C_6Br_5.OBr$ , of Benedikt.

By the action of bromine on symmetrical dichloraniline, tribromodichloraniline is formed; it crystallises in white needles (m. p.  $219^\circ$ ), and with amyl nitrite gives tribromodichlorobenzene, which crystallises in small needles.

The facts described in this paper are in perfect accordance with the generalisation enunciated above, and a table is given in which the results obtained by the author and other chemists on this point are collated.

V. H. V.

**Isobutylaniline.** By C. GIANNETTI (*Gazzetta*, 1882, 266—268).—The hydrobromide of this base is obtained, together with aniline hydrobromide and other products, by heating aniline with isobutyl bromide. The aniline hydrobromide separates in crystals; and on submitting the decanted liquid to a series of fractional distillations, isobutylaniline is ultimately obtained as an oily, nearly colourless liquid, boiling at  $242^\circ$ , and having a sp. gr. of 0.9262 at  $15^\circ$ . It darkens in colour by keeping, but not so much as aniline; has an empyreumatic odour like that of geranium leaves. It is very slightly soluble in water, 1 pt. requiring for solution 12,500 pts. water at  $15^\circ$ . It forms well crystallised salts; the platinochloride crystallises in golden-yellow prisms. With sodium hypobromite (Yvon's reagent), isobutylaniline gives a deep wine-red coloration; with calcium hypochlorite gradually a brownish tint, which disappears on adding an excess of the reagent.

H. W.

**Diphenylamine and Paraditolylamine.** By E. LELLMANN (*Ber.*, 15, 825—832).—*Benzoylmononitrodiphenylamine*,



is best prepared by slowly adding 50 grams of fuming nitric acid (sp. gr. 1.53) to a well cooled solution of 10 grams of benzoyldiphenylamine in 100 grams of glacial acetic acid. The mixture is left at rest for some time, and then water is added. On recrystallising the precipitated benzoylmononitrodiphenylamine from hot alcohol, it is obtained in yellow prisms (m. p.  $129^\circ$ ), soluble in glacial acetic acid. When this compound is treated with tin and hydrochloric acid, the nitro-group is simply converted into an amido-group; an anhydro-base is not formed. This shows that benzoylmononitrodiphenylamine (m. p.  $129^\circ$ ) is not an ortho-compound.

*Paranitrodiphenylamine*,  $NHPh.C_6H_4.NO_2$  (m. p.  $133^\circ$ ), obtained by the action of alcoholic potash on the above compound, is identical with Witt's nitrodiphenylamine from nitrosonitrodiphenylamine (*Ber.*, 11, 757; 12, 1399). Two isomeric dinitro-derivatives are formed when benzoyldiphenylamine is added to fuming nitric acid (sp. gr. 1.52). The crude product precipitated on the addition of water to the acid



mixture, is dried and treated with cold benzene (b. p. 80—85°), in which benzoylorthodinitrodiphenylamine is soluble. On dissolving the residue in boiling benzene, the para-compound is obtained in monoclinic crystals (m. p. 224°),  $\infty P$ : —  $P$ :  $OP$ .  $a$ :  $b$ :  $c$  1.4582: 1: 1.01295;  $\beta = 67^\circ 58' 11''$ . The crystals have a yellow colour and are highly refractive. They are sparingly soluble in alcohol and acetic acid. Alcoholic potash converts this substance into *paradinitrodiphenylamine*,  $NH(C_6H_4.NO_2)_2$  (m. p. 216°), which is identical with the compound obtained by Witt from nitrosodinitrophenylamine.

*Benzoylorthodinitrodiphenylamine* has not been prepared in a state of purity. On treatment with alcoholic potash, it yields orthodinitrodiphenylamine, which crystallises in needles (m. p. 220°) of a red colour.

*Benzoyldibromodiphenylamine*,  $PhCO.N(C_6H_3Br)_2$  (m. p. 142°), is deposited as a crystalline precipitate when bromine is added to a solution of benzoyldiphenylamine in glacial acetic acid. When this body is treated with alcoholic potash *dibromophenylamine*,  $NH(C_6H_4Br)_2$ , is formed. This substance is deposited from alcohol in lustrous prisms (m. p. 107°), soluble in alcohol and glacial acetic acid.

*Phthalyl-di-diphenylamine*,  $C_6H_4(CO.NPh_2)_2$ , formed by the action of phthalic chloride on diphenylamine, crystallises in prisms (m. p. 238°) soluble in alcohol.

*Benzoylmononitroparaditolylamine*,  $PhCO.N(C_6H_4Me)C_6H_3Me.NO_2$ , is prepared by slowly adding 20 grams of nitric acid (sp. gr. 1.53), diluted with an equal volume of glacial acetic acid, to 3 grams of benzoylditolylamine dissolved in 40 grams of acetic acid. The mixture is diluted with water, and the yellow precipitate which is thrown down is recrystallised from alcohol, when the benzoylnitroparaditolylamine is obtained in yellow prisms (m. p. 167°), soluble in alcohol and in glacial acetic acid.

*Mononitroparaditolylamine*,  $C_6H_4Me.NH.C_6H_3Me.NO_2$ , obtained by the action of alcoholic potash on the preceding compound, crystallises in red plates (m. p. 85°), which dissolve freely in the ordinary solvents.

Dinitroparaditolylamine forms brown plates (m. p. 191°).

W. C. W.

**Action of Phosphorus Pentachloride on Benzoyldiphenylamine.** By A. CLAUS and H. SCHAARE (*Ber.*, 15, 1285—1288).—By the action of phosphorus pentachloride on benzoyldiphenylamine, the authors obtained a dichloro-derivative, which they formerly considered to be dichlorobenzenyldiphenylamine, formed by the replacement of oxygen by two chlorine-atoms. But considering that the dichloro-derivative is difficult to obtain, that hydrochloric acid is evolved in its formation, and that the chlorine-atoms are not removed by boiling with alkali, the authors incline to the view that the dichloro-derivative is formed by the replacement of two hydrogen-atoms in diphenylamine hydrochloride. They find that the same compound is formed by the direct action of chlorine on benzoyldiphenylamine in chloroform solution, and analyses of the purified substance point to the formula  $(C_6H_4Cl)_2N.CO.Ph$ . By prolonged treatment with alkalis or alcoholic ammonia, the substance yields dichlorodiphenylamine,

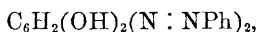
$\text{NH}(\text{C}_6\text{H}_4\text{Cl})_2$  and a salt of benzoic acid, a reaction which also points to the replacement of the hydrogen by chlorine. The authors propose to examine the action of phosphorus pentachloride on other secondary amines containing an acidic grouping, and especially on benzoylnaphthyl-derivatives, in order to determine the structural constitution of naphthalene. V. H. V.

**A New Class of Amidines.** By E. LELLMANN (*Ber.*, **15**, 832—834).—By the action of tin and acetic acid on benzoylorthamido-paraditolylamine, a molecule of water is expelled, and *paratolylbenzenyltolyleneamidine*,  $\text{C}_6\text{H}_4\text{Me.N} \begin{smallmatrix} \text{C}_6\text{H}_3\text{Me} \\ \text{C.C}_6\text{H}_5 \end{smallmatrix} \text{N}$ , is produced. This

base is deposited from alcohol in needles or prisms soluble in the ordinary solvents. The crystals melt at  $166^\circ$ , but after they have been fused two or three times the melting point sinks to  $160^\circ$ .

The hydrochloride crystallises with 1 mol. of water; the sulphate forms lustrous prisms. W. C. W.

**Nomenclature of Complicated Azo-compounds.** By K. HEUMANN (*Ber.*, **15**, 813—816).—The author proposes that the term *disazo*-compounds proposed by Wallach to denote a special class of azo-compounds, should be applied more generally to those compounds containing two azo-groups combined with the same hydrocarbon radicle. The name of the compound is then formed by placing before the term “disazo” the name of the hydrocarbon-radicle attached to the two azo-groups, and after it the names of the radicles combined with these groups. Thus *azobenzene-resorcinolazobenzene*,



then becomes *resorcinol-disazobenzene*, and its isomeride *azoazobenzene-resorcinol*,  $\text{Ph.N}_2\text{C}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_3(\text{OH})_2$ , would be styled *benzene-diazo-benzeneresorcinol*,  $\text{C}_6\text{H}_4 \begin{Bmatrix} \text{N}_2\text{Ph} \\ \text{N}_2\text{C}_6\text{H}_3(\text{OH})_2 \end{Bmatrix}$ .

Other instances are given of the application of this principle: thus phenolbidiazobenzene,  $\text{OH.C}_6\text{H}_3(\text{N}_2\text{Ph})_2$ , is styled *phenoldisazobenzene*, and azobenzenephloroglucol,  $(\text{Ph.N}_2)_2\text{C}_6\text{H}(\text{OH})_3$ , *phloroglucoldisazobenzene*. Compounds containing three azo-compounds would in a similar manner be styled trisazo-compounds. P. P. B.

**Preparation of Azoxybenzene.** By H. KLINGER (*Ber.*, **15**, 865—867).—The best method for preparing azoxybenzene is to boil a solution of 10 parts of sodium in 250 of methyl alcohol with 30 parts of pure nitrobenzene, in a flask fitted with an upright condenser. When the reaction is complete, the methyl alcohol is distilled off, and sufficient water is added to dissolve the sodium formate which is produced. The azoxybenzene is obtained as an oily liquid, which rapidly solidifies to a crystalline mass.

If ethyl alcohol is substituted for methyl alcohol in this process, a very poor yield of azoxybenzene is obtained.

By the action of sodium methylate on para- and ortho-nitrotoluenes, red amorphous bodies are produced. W. C. W.

### Molecular Rearrangement of certain Hydrazo-compounds.

By G. SCHULTZ (*Berl. Ber.*, **15**, 1539).—This is a preliminary notice of the results of investigations of the transformation of certain aromatic hydrazo-compounds into the isomeric diphenyl-bases. The conversion was effected by treating the azo-bodies, in alcoholic solution, with stannous chloride. In the case of bodies of the ortho- and meta-series the conversion takes place smoothly and rapidly on warming the solution. The para-compounds are best converted by allowing the solution to stand for a long time in contact with stannous chloride. Azo-compounds which contain hydroxyl or amido-groups are not converted into diphenyl bases, but are decomposed at the point of union of the nitrogen atoms.

Di-metachlorazobenzene and di-parachlorazobenzene yield the corresponding diphenyl bases; orthazo-ethylbenzene (m. p. 47°) yields diamidodiethyl-diphenyl. These, together with a number of incidental observations, will be made the subject of a fuller communication.

C. F. C.

### Orthotolyldiazine. By M. BÖSLER (*Annalen*, **212**, 338—339).—

This base, prepared in the same manner as phenylhydrazine, and purified by distillation and subsequent crystallisation from hot light petroleum (b. p. 70—100°), forms colourless oblique tabular crystals melting at 56°, and having the composition  $C_7H_7.N_2H_3$ . By oxidation in the air, it is slowly converted into a brown oil. It dissolves readily in alcohol, ether, and chloroform, sparingly in cold light petroleum. With mineral acids it forms stable well crystallised salts. The *hydrochloride*,  $C_7H_{10}N_2.HCl + H_2O$ , is sparingly soluble in strong hydrochloric acid, easily in water and in alcohol, and crystallises in white silky needles, which give off their water at 100°. The *nitrate*,  $C_7H_{10}N_2.HNO_3$ , forms thin anhydrous laminae, very soluble in water and in alcohol, and precipitated from the alcoholic solution by ether.

H. W.

### Di- and Tri-phenyl Phosphines. By A. MICHAELIS and L.

GLEICHMANN (*Ber.*, **15**, 801—804).—*Diphenylphosphine*,  $Ph_2PH$ , is formed by decomposing diphenylphosphine chloride with water or caustic soda, thus: A portion of the phosphine chloride yields the compound  $Ph_2P.OH$ , which is resolved at the ordinary temperature into a further quantity of diphenylphosphine and diphenylphosphinic acid:  $2(Ph_2P.OH) = Ph_2PH + Ph_2PO.OH$ . Diphenylphosphine is a liquid which absorbs oxygen slowly from the air and combines directly with chlorine. It is a weak base, its salts are decomposed by water, and it boils at 280°.

*Triphenylphosphine*,  $Ph_3P$ , is obtained by the action of sodium upon a mixture of phosphenyl chloride and bromobenzene diluted with ether. On evaporating the ethereal solution, after the removal of sodium chloride and bromide, the triphenylphosphine is obtained as a white crystalline mass. It is insoluble in water, but soluble in other ordinary solvents; it crystallises in large transparent prisms or tables melting at 75—76°, and may be distilled in an atmosphere of

hydrogen. When heated at  $76^{\circ}$  in contact with the air, it does not oxidise, but if the temperature be raised, it burns with a smoky flame. It is a weak base, forming a hydriodide which is decomposed by water. With chlorine it forms a compound, which when treated with caustic soda, forms *triphenylphosphonium hydroxide*,  $\text{Ph}_3\text{P}(\text{OH})_2$ . This compound crystallises in long thin white prisms, melting at  $148^{\circ}$ . When heated at  $100^{\circ}$  it is resolved into water and *triphenylphosphinic oxide*,  $\text{Ph}_3\text{PO}$ .

*Triphenylphosphine sulphide*,  $\text{Ph}_3\text{PS}$ , is formed by the direct union of sulphur and triphenyl phosphine; it crystallises from alcohol in long brilliant needles, insoluble in water and ether, melting at  $150$ — $151^{\circ}$ .

*Triphenylmethyl-phosphonium iodide*,  $\text{Ph}_3\text{PMeI}$ , is obtained by the action of methyl iodide on triphenylphosphine, and forms shining leaflets (m. p.  $165$ — $166^{\circ}$ ). Triphenylphosphine unites with methylene iodide and ethylene bromide, forming *methylene-hexaphenylphosphonium iodide*,  $\text{CH}_2 : (\text{PPh}_3\text{I})_2$ , melting at  $230$ — $231^{\circ}$ , and *ethylene-hexaphenylphosphonium bromide*,  $\text{C}_2\text{H}_4(\text{PPh}_3\text{Br})_2$ , at  $300^{\circ}$  respectively.

Triphenylphosphine unites directly with mercuric chloride, forming a crystalline compound. P. P. B.

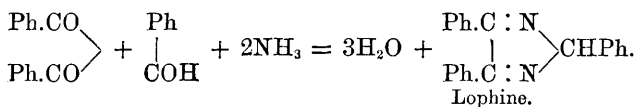
**Synthesis of Tyrosine.** By E. ERLÉNMEYER and A. LIPP (*Ber.*, **15**, 1544).—Tyrosine has been obtained hitherto only as a product of decomposition of proteïds; after a long series of attempts, the authors have devised a method which contains at least the promise of its synthetical production. Phenylamine was converted into paranitrophenylamine, then into the corresponding amido-compound, and this, by the action of nitrous acid, into parahydroxyphenylactic acid and a substance which remained in aqueous solution after exhaustion of the former by means of ether. The aqueous solution was supersaturated with ammonia and evaporated, yielding a crystalline mass having all the characteristic properties of tyrosine.

Regarding the constitution of tyrosine, Barth long since (*Annalen*, **152**, 100) inferred it to be parahydroxyphenylamidopropionic acid; the methods proposed by him (*ibid.*, **163**, 296) and by Beilstein (*ibid.*, **163**, 142), however, for its preparation are imperfect, in failing to recognise tyrosine as the  $\alpha$ -amido-acid, which identity the authors have established.

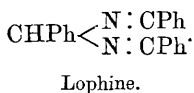
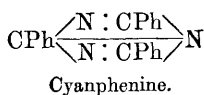
A fuller communication on the subject, of which this is only a preliminary notice, is promised, together with incidental observations on several new compounds, *e.g.*, parathiophenylalanine, para- and ortho-nitrophenyl,  $\alpha$ -nitroxypropionic acid, paramidophenylactic acid, hydroxyhydrocarbostyryl, and paramidophenylalanine. C. F. C.

**Constitution of Lophine and Allied Compounds.** By B. RADZISZEWSKI (*Ber.*, **15**, 1493).—The author anticipates in this paper the more extended publication of the results of his investigation of this subject, in consequence of the appearance of a paper by Japp and Robinson (*Trans.*, 323) on lophine and amarine. Lophine has hitherto been obtained either from amarine, whose constitution is

unknown, or by means of a reaction at a temperature above that at which it can be assumed to occur smoothly. In his endeavours to obtain lophine by a method free from these objections, the author has arrived at the following results:—Cyanphenine, prepared by Cloez's method, reacts with nascent hydrogen to form ammonia and lophine, both in the wet way (warming its solution in acetic acid with zinc), and on distilling it with potash and iron filings. By the former method, the theoretical yield is obtained, the lophine being easily isolated by precipitating its acetic solution with water, after the removal of the zinc. The constitution of cyanphenine being as yet problematical, nothing is hereby established in regard to the question at issue beyond the genetic connection of cyanphenine with lophine. More valuable evidence is afforded by the formation of lophine, in approximately theoretical quantity, by the interaction of benzil, benzaldehyde, and ammonia in alcoholic solution. The most probable expression of the reaction is the following:—



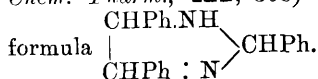
and such being the probable constitution of lophine, the generally accepted formula of cyanphenine,  $\text{PhC} \begin{array}{c} \diagup \text{N-CPh} \\ \diagdown \text{N=CPh} \end{array} \text{N}$ , would appear to be no longer tenable; and indeed, further, this formula can scarcely be reconciled with the fact of the conversion of one only of the three nitrogen-atoms into ammonia by the action of nascent hydrogen. The author therefore formulates cyanphenine and lophine as follow:—



This view of the constitution of lophine is further supported by the fact of its decomposition by potash into benzyl alcohol and benzoic acid, *i.e.*, in the first instance, benzaldehyde. The author further has reason for regarding the constitution of glyoxaline as analogous to that of lophine, as expressed by the following formula:—  
 $\begin{array}{c} \text{CH : N} \\ | \\ \text{CH : N} \end{array} \text{CH}_2$ . Its formation by the interaction of formaldehyde, glyoxal, and ammonia, is especially suggestive of a constitution analogous to that of lophine.

(3.) The formation of amarine by the interaction of benzoin, benzaldehyde, and ammonia is suggestive of the constitution represented by the formula  $\begin{array}{c} \text{CHPh.NH} \\ \diagdown \text{CHPh : N} \end{array} \text{CHPh}$ . The author is also of opinion that the nearly related substance isolated by Kühn (*Ann.*

*Chem. Pharm.*, **122**, 308) is a hydroamarine represented by the



C. F. C.

**Occurrence of Carvacrol in the Ethereal Oil of Garden Sage (*Satureia Hortensis*).** By E. JAHNS (*Ber.*, **15**, 816—819).—This oil is a yellow mobile liquid having an odour resembling that of thymol, and exhibiting feeble laevogyrate properties. Its refractive index for D is 1.493 at 15°, and its sp. gr. is 0.898 at 15°. The sample investigated had the following percentage composition:—Carvacrol, 30; cymene, 20; and a terpene (b. p. 178—180°), 50. The presence of a small quantity of a phenol producing a violet coloration in solutions of ferric chloride, was also observed. The author finds that, contrary to the generally accepted statements, carvacrol produces a green coloration in solutions of ferric chloride. The following physical constants of the terpene formed in the oil have been determined:—Sp. gr. = 0.855 at 15°; refractive index = 1.481. Carvacrol occurs also in *origanum* oil and in the oil of *Thymus Serpyllum*, in the latter it is accompanied by thymol.

P. P. B.

**A Polymeride of Toluquinone.** By G. SPICA (*Gazzetta*, 1882, 225—227).—When toluquinone is treated with sulphuric acid diluted with an equal weight of water, it gradually dissolves, the solution turning brown and depositing a nearly black pulverulent substance, very slightly soluble in water, insoluble in benzene, very soluble in ether and in alcohol, moderately soluble in acetic acid. When purified by solution in this acid, precipitation by water and washing in a percolator with chloroform, it gave by analysis numbers agreeing very nearly with the formula of toluquinone,  $\text{C}_6\text{H}_3\text{MeO}_2$ , but melted at 300°, whereas toluquinone itself melts at 64°. Hence it appears to be a polymeride of toluquinone.

This polymeride, suspended in water and subjected for several days to a current of sulphur dioxide, is converted into a hydroxy-derivative,  $[\text{C}_6\text{H}_3\text{Me}(\text{OH})(\text{OH})]_n$ , which crystallises, on evaporating the resulting solution under reduced pressure, in fibrous tufts of white nacreous needles melting at 204°, very soluble in ether and in alcohol, soluble also in benzene. It is somewhat unstable, and on exposure to air and moisture is gradually reconverted into the polymeric toluquinone.

H. W.

**Purpurogallin.** By P. DE CLERMONT and P. CHAUTARD (*Compt. rend.*, **94**, 1362—1364).—Purpurogallin, obtained from pyrogallol by the action of oxidising agents or of gum arabic, or by passing air through an aqueous solution in presence of platinum-black, crystallises from alcohol in velvety needles of dark-brown colour melting at 256° and subliming with decomposition at a slightly higher temperature.

*Sodium purpurogallate*,  $\text{C}_{20}\text{H}_{12}\text{Na}_4\text{O}_9$ , is formed by mixing alcoholic solution of purpurogallin and soda; it is very deliquescent, crystallises with difficulty in prismatic needles, very soluble in water, insoluble in alcohol and other solvents. On heating it with ethyl iodide under pressure, the ethyl-derivative is obtained.

*Barium purpurogallate*,  $C_{20}H_{12}Ba_2O_9$ , is precipitated in crystalline plates, when barium chloride is added to a solution of the sodium compound: it is almost insoluble in water and other solvents, and is decomposed by acids.

When ammonia is added to purpurogallin suspended in water, the mixture assumes successively a green, a blue, and a yellow colour. On evaporating the solution to dryness and treating the residue several times with alcohol and ether, an insoluble portion is obtained, consisting probably of an amido-compound and an oxide of purpurogallin. This compound is soluble in water, nearly insoluble in alcohol, and completely insoluble in other solvents.

By adding an excess of bromine, drop by drop, to purpurogallin suspended in acetic acid, a *tetrabromo-compound*,  $C_{20}H_{12}Br_4O_9$ , is obtained, crystallising in red transparent needles (m. p.  $202-204^\circ$ ) which darken in colour on exposure to air. It dissolves with yellow colour in alcohol, ether, and acetic acid, with a violet colour in benzene and chloroform. Nitric acid and alkalis decompose the bromo-compound, whilst it is dissolved by sulphuric acid without decomposition and with a red colour. Chlorine and iodine under similar circumstances give crystalline compounds with purpurogallin.

Hydrochloric acid does not act on purpurogallin, but sulphuric acid dissolves it in the cold, yielding a purple solution from which it is precipitated unaltered by water: on heating the solution, sulphurous anhydride is evolved, and the compound  $C_{20}H_{12}O_{10}$  formed, which crystallises in long brown needles, giving with ammonia a violet coloration, and blue with potassium and sodium hydroxide.

Hydriodic acid heated with purpurogallin under pressure acts on it slowly, forming a series of hydrocarbons of the general formula  $(C_{10}H_{14})_n$ . The first hydrocarbon boils at  $195^\circ$ , and appears to belong to the cymene group, although it differs in its properties from the known members of that group. A little above  $360^\circ$  a hydrocarbon of the formula  $C_{20}H_{28}$  is obtained as a viscous liquid. A third hydrocarbon distils at the melting point of glass.

*Tetracetyl purpurogallin*,  $C_{20}H_{12}Ac_4O_9$ , is obtained by heating purpurogallin with acetic anhydride at  $140^\circ$ . It crystallises in prismatic needles melting at  $186^\circ$ , and subliming at a little above that temperature; when moist, the crystals are brown, but in the dry state they are of a brilliant golden yellow. It is insoluble in water, but soluble in alcohol and ether; with ammonia, soda, and potash it gives reactions similar to those of purpurogallin, into which it is converted by heating with an excess of barium hydroxide under pressure. L. T. O'S.

**A New Class of Colouring-matters.** By O. FISCHER and C. RUDOLPH (*Ber.*, 15, 1500-1505).—The authors have investigated "Flavaniline," the characteristic product of the action of zinc chloride at  $250-270^\circ$ ; on acetanilide. The colouring-matter, which dyes silk bright yellow with a moss-green fluorescence, is the monacid salt of a strongly diacid base, which is thrown down by ammonia from a solution of the former, as a milky precipitate which ultimately takes the form of long needles. These are slightly soluble in water, freely in alcohol; they melt at  $97^\circ$ , the colour changing to yellow.

The empirical composition of the base is represented by the formula  $C_{16}H_{14}N_2$ , and its formation from acetanilide therefore by the equation:  $2C_8H_9NO = C_{16}H_{14}N_2 + 2H_2O$ . The base is not affected by nascent hydrogen ( $Sn + HCl$ ). The di-acid salt is prepared by pouring the aqueous solution of the monacid salt into cold concentrated hydrochloric acid, in which it is almost insoluble. It is dissolved by water with re-formation of the monacid salt. The platinochloride,  $C_{16}H_{14}N_2 \cdot 2HCl \cdot PtCl_4$ , was obtained by adding the solution of the base in hot concentrated hydrochloric acid to a platinum chloride solution.

*Ethylflavaniline* was obtained by heating an alcoholic solution of the base with ethyl iodide at  $110^\circ$ . Red needles separated on cooling, and were purified by recrystallisation from dilute hydriodic acid. The resulting compound is the hydriodate of monoethylflavaniline,  $C_{16}H_{13}EtN_2 \cdot HI$ : the base is precipitated by ammonia from the solution of this salt as a colourless resinous mass. Its salts have a redder tone than the corresponding salts of flavaniline, and dye silk orange.

*Phenylflavaniline* is obtained by heating the base with aniline and benzoic acid at  $170^\circ$ . Its salts crystallise well, and are yellow coloured.

*Reaction with Nitrous Acid.*—On adding sodium nitrite to a solution of the monacid salt, a diazoamido-compound is thrown down as a yellowish-red crystalline precipitate. If the decomposition be effected, with suitable precautions, in presence of excess of acid, a phenol is obtained, and may be isolated in the form of colourless plates melting at  $238^\circ$  and subliming without decomposition. According to analysis its empirical formula is  $C_{16}H_{13}NO$ . It possesses both acid and basic properties, and its salts are beautifully crystalline. On distillation with zinc-dust, the phenol is converted into a new base, *flavoline*,  $C_{15}H_{13}N$ , which distils above  $360^\circ$  as a yellowish oil; on exposure to a freezing mixture the oil solidifies to a mass of four-sided plates melting at  $65^\circ$ . The picrate and the chromate of this base are very insoluble. Its nitrogen-atom is not attacked by nitrous acid. The authors regard it as a derivative of quinoline, and flavaniline as a monamido-derivative of flavoline, in support of which they cite the result of the nitration and amidation of the base, whereby they obtained a colouring-matter which appeared to be identical with flavaniline.

The further investigation of this base as the type of a new series is in progress. C. F. C.

**New Colouring-matters.** By J. v. HOERMANN (*Ber.*, **15**, 1541—1544).—By the action of epichlorhydrin on aniline and its homologues, the author has obtained a series of bodies which, on oxidation with chloranil, yield true colouring-matters; these, however, are of little technical value owing to their being decomposed by boiling with water. The reaction by which they are formed was suggested by the analogous reaction of ethylene oxide with aromatic amines, which has been investigated by Demole. From an *à priori* investigation of the reaction, the author regards the products as containing a quinoline nucleus, and the colouring-matters as related to cyanin. Epichlorhydrin reacts



also with secondary bases, but with difficulty, requiring prolonged heating at a high temperature (150—160°) to complete the reaction.

C. F. C.

**$\beta$ -Naphthoxyl Aldehyde.** By G. KAUFMANN (*Ber.*, **15**, 804—807).—The product of the action of caustic soda and chloroform on  $\beta$ -naphthol, yields on treatment with light petroleum, an insoluble grey powder, which, when crystallised from aniline, forms small brownish prisms melting at 210°. This substance is identical with that described by Rousseau (*Compt. rend.*, **94**, 133), as a pseudo-diatomic alcohol. The portion soluble in light petroleum consists of two compounds, viz.,  $\beta$ -naphthoxyl-aldehyde and a small quantity of a substance insoluble in caustic soda, which crystallises from a mixture of ether and alcohol in slender shining needles, melting at 144°.

$\beta$ -Naphthoxyl aldehyde,  $C_{10}H_6(OH).COH$ , is insoluble in water, but soluble in alcohol and ether, and forms colourless prisms melting at 76°. Its solutions give a brown coloration with ferric chloride, and reduce ammoniacal solutions of silver nitrate; it is soluble in caustic alkalis, forming with caustic soda the compound  $C_{10}H_6(ONa).COH$ , which crystallises in yellow leaflets. By careful fusion with caustic potash this aldehyde is oxidised to naphthoxyl-carboxylic acid, its production being attended with the formation of some *dinaphthol*.

Naphthoxyl-carboxylic acid,  $C_{10}H_6(OH).COOH$ , is sparingly soluble in water, and crystallises from dilute alcohol in fine needles, melting at 150°; its alcoholic solution gives a blue coloration with ferric chloride. This acid, when boiled with water, is resolved into carbonic anhydride and  $\beta$ -naphthol. It forms crystalline potassium and ammonium salts, and its silver salt is obtained as a white amorphous precipitate. This acid is isomeric with the two described by Schäffer (*Annalen*, **152**, 279) and the four acids described by Stumpf (*ibid.*, **188**, 1), and is regarded by the author as a  $\beta\beta$ -derivative.

The *dinaphthol*,  $(C_{10}H_6.OH)_2$ , formed together with the above acid, is insoluble in water, but soluble in alcohol, from which it crystallises in slender silky needles, melting at 195°. It is soluble in alkalis, but insoluble in solutions of alkaline carbonates. It produces no coloration with solutions of ferric chloride, and is an isomeric of the two *dinaphthols* which Dianin obtained by the action of ferric chloride on naphthol (*Ber.*, **6**, 1252).

Attempts made to prepare naphthoxyl aldehydes from  $\alpha$ -naphthol yielded unsatisfactory results.

P. P. B.

**Hydrazine-benzoic Acids.** By E. FISCHER and E. RENOUF (*Annalen*, **212**, 333—338).—The ortho- and meta-acids are already known (*Annalen*, **180**, 1:2; *Ber.*, **13**, 679; *Abstr.*, 1880, 647). The ortho-acid, as might be expected, is the only modification convertible by separation of water into a simple anhydride.

This compound,  $C_7H_6N_2O = C_6H_4 < \begin{smallmatrix} CO \\ NH \end{smallmatrix} > NH$ , is prepared by heating the ortho-acid as quickly as possible to 220—225°, interrupting the operation as soon as the mass is completely fused, and no more water

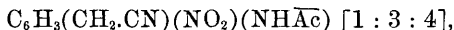
escapes. It is quite colourless when pure, and separates from the hot alcoholic solution on slow cooling in shining mostly six-sided monoclinic plates, often arranged in parallel rows, and exhibiting the combination  $OP \cdot \infty P \infty \cdot P$ . The  $P$ -faces, like all the rest, are highly lustrous and specular, but always much arched. Cleavage very distinct, parallel to the orthopinacoid. The compound has no definite melting point. It begins to sinter together and becomes coloured at  $220^\circ$ ; melts completely with progressive decomposition at  $242^\circ$  to a dark-red liquid; and is converted after some time at the same temperature into a tarry mass. It exhibits both basic and acid properties; dissolves readily in alkalis; and in boiling aqueous solution slowly decomposes the carbonates of the alkaline earths. On mixing its concentrated solution in pure soda-ley with absolute alcohol, the sodium salt,  $C_7H_6N_2ONa$ , separates in fine silvery laminæ containing crystal-water which escapes at  $100^\circ$ , the crystals at the same time losing their lustre. Equal stability is exhibited by the compounds of the anhydride with strong acids. The *hydrochloride*  $C_7H_6N_2O \cdot HCl$  forms white needles very soluble in water and in alcohol, much less soluble in strong hydrochloric acid. The *sulphate* exhibits similar properties. The anhydride likewise unites with *metallic salts*. On mixing its cold aqueous solution with mercuric chloride, a white flocculent precipitate is formed which dissolves in hot water, and the solution, on cooling, deposits tufts of needles having the composition  $C_7H_6N_2O \cdot HgCl_2$ . A similar compound is formed with silver nitrate.

A *diacetyl derivative*,  $C_6H_4 < \begin{smallmatrix} CO \\ NAc \end{smallmatrix} > NAc$ , is formed on boiling the anhydride with five times its weight of acetic anhydride, and crystallises from hot alcohol in white needles melting at  $112^\circ$ , very slightly soluble in water and dilute acids, but dissolved and decomposed by hot alkaline leys. Two ethyl-derivatives are also formed on heating the sodium salt with ethyl iodide and a small quantity of alcohol, one soluble in alcohol, the other insoluble and apparently consisting of a diethyl-compound.

*Parahydrazine-benzoic acid*,  $C_7H_6N_2O_2 = COOH \cdot C_6H_4 \cdot NH \cdot NH_2$ , is prepared by drenching 7 parts paramidobenzoic hydrochloride with 5 parts strong hydrochloric acid (sp. gr. 1.19) and 30 parts water, gradually adding to the cooled mixture the calculated quantity of sodium nitrite, the amido-acid being thereby completely converted into the diazo-compound and dissolved; and on pouring the liquid into a cold saturated solution of normal sodium sulphite containing rather more than 2 mols. of the salt to 1 mol. of the amido-acid, then adding acetic acid to acid reaction, and zinc-dust, warming gently till the solution becomes colourless, and passing hydrogen chloride into the perfectly cooled liquid, the hydrochloride of the hydrazine-acid separates, together with sodium chloride. The saline mass is then to be washed with cold water, and the residue recrystallised from hot water. The salt thus obtained forms white needles slightly soluble in cold, moderately soluble in hot water, and having, when dried at  $100^\circ$ , the composition  $C_7H_6N_2O_2 \cdot HCl$ . The free *hydrazine-acid* obtained by dissolving this salt in soda-ley and precipitating with acetic acid, has, after drying in a vacuum, the composition  $NH_2 \cdot NH \cdot C_6H_4 \cdot COOH$ . It

is very slightly soluble in cold, much more readily in hot water, and crystallises from the warm aqueous solution on rapid cooling in slender needles, and on slow cooling in larger colourless plates. Heated in a capillary tube, it melts at 220—225°, with brisk intumescence, and partial resolution into carbonic anhydride and phenylhydrazine. H. W.

**Phenylacetic Acid.** By S. GABRIEL (*Ber.*, 15, 834—842).—*Paramidobenzyl cyanide*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CN}$ , is best prepared by the action of tin and hydrochloric acid on nitrobenzyl cyanide (m. p. 116°). After precipitating the tin from the solution by sulphuretted hydrogen, the filtrate is mixed with an excess of sodium hydroxide and extracted with ether. On evaporating the ethereal extract, the cyanide remains in crystalline plates (m. p. 44°), which are sparingly soluble in carbon bisulphide, but dissolve freely in most solvents. The *diacetic* derivative,  $\text{N}\bar{\text{A}}\text{c}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CN}$ , forms needle-shaped crystals (m. p. 153°) soluble in chloroform, ether, benzene, carbon bisulphide, acetic acid, and in hot water. *Paracetamidobenzyl cyanide*,  $\text{NH}\bar{\text{A}}\text{c}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CN}$ , which is formed together with the preceding compound, crystallises in colourless needles (m. p. 96°), soluble in alcohol, ether, glacial acetic acid, and chloroform. By the action of strong nitric acid on either of these *acetic* derivatives, *metanitroparacetamidobenzyl cyanide*,



is produced. It crystallises in yellow needles or plates which melt at 113°, and dissolve readily in benzene, chloroform, and warm acetic acid. On saponification with concentrated hydrochloric acid this compound yields *nitramidophenylacetic acid*,  $\text{C}_6\text{H}_3(\text{CH}_2\cdot\text{COOH})(\text{NO}_2)(\text{NH}_2) [1 : 3 : 4]$ . This acid crystallises in orange-coloured needles melting at 144°, freely soluble in alcohol, ether, acetic acid, ammonia, and in hot water. The hydrochloride is decomposed by water. When a solution of the acid in ether and alcohol is mixed with amyl nitrite and strong hydrochloric acid, red needles of nitrosomethylnitrodiazobenzene chloride are deposited. The crystals explode when heated. The diazo-compound is decomposed by alcohol with the formation of nitrosomethylmetanitrobenzene (m. p. 115—118°), which crystallises in needles soluble in alcohol, ether, acetic acid, benzene, chloroform, and in soda. On oxidation with chromic mixture, *metanitrobenzaldehyde* (m. p. 57°), is produced.

*Metanitroparamidobenzyl cyanide* is prepared by adding soda to an aqueous solution of nitroacetamidobenzyl cyanide, in quantity sufficient to produce a decidedly alkaline reaction. Orange-coloured rhombic plates (m. p. 118°) are deposited, which dissolve readily in alcohol, ether, and acetic acid. A diazo-compound appears to be formed by the action of nitrous acid on the nitric acid solution of the cyanide.

*Bromacetamidobenzyl cyanide* (m. p. 129°), prepared by the action of bromine-water on paracetamidobenzyl cyanide, yields *metabromoparamidophenylacetic acid* when saponified with strong hydrochloric acid. This acid crystallises in colourless scales melting at 136°, soluble in ether, alcohol, benzene, and acetic acid. The *diazo*-compound was not

isolated, but the product of its decomposition by alcohol was shown to be metabromophenylacetic acid melting at  $100.5^{\circ}$ . W. C. W.

**$\alpha$ -Ditolylpropionic Acid.** By A. HAISS (*Ber.*, **15**, 1474—1481).—The author prepared this acid by Böttinger's method (*ibid.*, 1595), and obtained by the action of sulphuric acid on 10 grams of pyrrocemic acid and 30 grams of toluene, a yield of 22 grams of the pure acid. It melts at  $151^{\circ}$ , and volatilises unchanged on raising the temperature. Details of crystallographic measurements are given. The ammonium salt crystallises from alcohol in long needles; on recrystallisation, it loses ammonia. The calcium salt forms a crystalline powder, sparingly soluble in water and alcohol. The ethyl salt crystallises from alcohol in prisms which melt at  $145^{\circ}$ .

*Ditolyethane*,  $\text{CHMe}(\text{C}_7\text{H}_7)_2$ . On distilling the acid with quicklime, it is converted, without carbonisation, into ditolyethane, boiling at  $294^{\circ}$ , and converted by oxidation into ditolylketone melting at  $94^{\circ}$ —identical therefore with Fischer's paratolyldiethane (*ibid.*, **7**, 1193).

*Dinitro- $\alpha$ -ditolylpropionic Acid.*—This nitro-acid is prepared by slowly adding  $\alpha$ -ditolylpropionic acid to a well cooled ( $-5^{\circ}$ ) mixture of nitric and sulphuric acids. After purification, it is obtained in yellowish crystals (m. p.  $129^{\circ}$ ), which are easily soluble in alcohol and in ether. The ammonium salt is prepared by dissolving the acid in alcoholic ammonia; from this solution, the calcium and barium salts are thrown down, as crystalline precipitates, on adding the chlorides. The corresponding diamido-acid is obtained by reduction with tin and hydrochloric acid in the usual way: on adding alcohol to the concentrated aqueous solution, the hydrochloride is precipitated in transparent needles.

*Tetranitro- $\alpha$ -ditolylpropionic Acid.*—For the formation of this compound a mixture of 2 vols. concentrated nitric acid and 1 of sulphuric, at  $15^{\circ}$  is requisite. The product crystallises in bright yellow needles melting at  $224^{\circ}$ , easily soluble in alcohol and in ether. The ammonium salt was prepared by dissolving the nitro-acid in alcoholic ammonia; it crystallises in bright yellow needles; the barium salt is easily soluble in water.

*Monobromo- $\alpha$ -ditolylpropionic Acid.*—This compound is obtained by adding bromine to a solution of the ditolylpropionic acid in chloroform and applying a gentle heat. It crystallises in warty masses melting at  $144^{\circ}$ , freely soluble in alcohol and in ether.

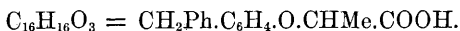
*Diphenylethanedetricarboxylic Acid.*—This acid is the product of the action of potassium permanganate on the ditolylpropionic acid, in boiling aqueous solution. It crystallises in shining needles melting at  $254^{\circ}$ , slightly soluble in water, easily in alcohol and in ether. On warming with concentrated nitric acid it is dissolved, but without change, and separates out on cooling. The ammonium salt of this acid crystallises in colourless needles. The barium salt is obtained as a crystalline precipitate, somewhat soluble in boiling water; the silver salt also is but slightly soluble in boiling water; the mercuric salt is soluble in water and in alcohol. The disodium salt is obtained by boiling a solution of soda with excess of the acid; the corresponding silver salt is easily soluble in hot water. The proof of the constitu-

tion of this acid lay in its conversion, by sublimation at  $280^{\circ}$ , into diphenylethanedicarboxylic acid melting at  $275^{\circ}$ , and the conversion of this by distillation from soda-lime into diphenylethane, boiling at  $286^{\circ}$ , and possessing all the properties of that prepared from aldehyde.

C. F. C.

**Benzyloxyphenyl- $\alpha$ -propionic and Benzylparamethyloxyphenyl- $\alpha$ -propionic Acid.** By M. MAZZARA (*Gazzetta*, 1882, 261—266).—The former of these acids was obtained by a process analogous to that previously employed for the preparation of benzyloxyphenylacetic acid (this vol., p. 403), viz., by heating potassium-benzylphenol in molecular proportion with the sodium salt of  $\alpha$ -chloropropionic acid (prepared by distilling calcium lactate with 2 mols.  $\text{PCl}_5$ , decomposing the crude distillate of lactic chloride with water, agitating the product with ether, and purifying the acid thereby dissolved by rectification).

On dissolving the product in water, and treating the solution with hydrochloric acid, an oily substance separated which soon solidified; and on treating this product with ammonium carbonate to remove a small quantity of unaltered phenol, and again adding hydrochloric acid, benzyloxyphenyl- $\alpha$ -propionic acid was precipitated in the crystalline state. This acid, purified by recrystallisation from dilute alcohol or hot water, crystallises in small shining scales melting at  $100$ — $102^{\circ}$ . It is very soluble in alcohol and ether, and produces a yellowish turbidity with picrates. It gives by analysis 74.72 per cent. carbon and 6.66 hydrogen, agreeing with the formula—



The *lead salt*,  $(\text{C}_{16}\text{H}_{15}\text{O}_3)_2\text{Pb.H}_2\text{O}$ , obtained by adding lead nitrate to a solution of the acid neutralised with ammonia, is a white flocculent precipitate, composed of minute needles. It is very slightly soluble in water, and becomes pasty under boiling water. Heated in a tube nearly to  $100^{\circ}$ , it melts and solidifies to a yellowish amorphous mass. The *barium salt*,  $(\text{C}_{16}\text{H}_{15}\text{O}_3)_2\text{Ba.H}_2\text{O}$ , is likewise a flocculent precipitate composed of small needles, which melts and gelatinises under boiling water; behaves like the lead salt, when heated in a tube at  $100^{\circ}$ . The *silver salt*,  $\text{C}_{16}\text{H}_{15}\text{O}_3\text{Ag}$ , is a white, apparently curdy precipitate, but little altered by light, sparingly soluble in alcohol and ether.

*Benzylparamethyloxyphenyl- $\alpha$ -propionic acid,*



is prepared like the preceding acid, but is very difficult to purify, being precipitated from its salts in a pasty condition, which it maintains for a long time. From boiling water, however, in which it is very slightly soluble, it may be obtained in small perfectly white crystals. It melts at  $115^{\circ}$ ; produces a yellowish turbidity with ferric salts. Its *lead salt*,  $(\text{C}_{17}\text{H}_{17}\text{O}_3)_2\text{Pb.H}_2\text{O}$ , is prepared like that of the preceding acid, which it resembles. The *barium salt*, obtained by precipitation from the ammonium salt, is very unstable. The *silver salt*

is but little altered by light. It is insoluble in water, softens and blackens under boiling water; dissolves in alcohol and in ether, and separates from the ethereal solution in scales. H. W.

**Hydrocinnamic Acid.** By S. GABRIEL and H. STEUDEMANN (*Ber.*, **15**, 842—847).—*Paramidohydrocinnamic acid* (m. p.  $131^{\circ}$ ) is formed by boiling an ammoniacal solution of paranitrohydrocinnamic acid (m. p.  $163^{\circ}$ ) with a solution of ferrous sulphate. (The reduction is complete when the precipitate, which is produced on the addition of hydrochloric acid to the concentrated filtrate, redissolves in an excess of acid.) The mixture is filtered, the filtrate concentrated and neutralised with hydrochloric acid to precipitate amidohydrocinnamic acid.

*Paracetamidohydrocinnamic acid*,  $\text{NH}_4\text{Ac} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_2\text{H}_4 \cdot \text{COOH}$ , crystallises in colourless needles (m. p.  $143^{\circ}$ ), soluble in alcohol, ether, and acetic acid. On the addition of potassium nitrate to a solution of the acetic derivative in sulphuric acid, *metanitroparacetamidohydrocinnamic acid*,  $\text{C}_6\text{H}_3(\text{C}_2\text{H}_4 \cdot \text{COOH})(\text{NO}_2)(\text{NHAc})$  [1:3:4], is produced. It is precipitated on diluting the acid solution. The best yield is obtained when not more than 1 gram of the substance is operated on. The nitro-compound forms pale yellow needles (m. p.  $174^{\circ}$ ), soluble in hot water, alcohol, benzene, and glacial acetic acid. When it is boiled with concentrated hydrochloric acid, *metanitroparamidohydrocinnamic acid*,  $\text{C}_6\text{H}_3(\text{C}_2\text{H}_4 \cdot \text{COOH})(\text{NO}_2)(\text{NH}_2)$  [1:3:4], is obtained. This acid forms orange-coloured crystals (m. p.  $145^{\circ}$ ), which dissolve freely in ether, acetic acid, and warm alcohol or water.

By the action of ethyl nitrite, it yields a *diazo*-, and not a nitroso-compound. The diazo-derivative is decomposed by boiling alcohol with formation of *metanitrohydrocinnamic acid* melting at  $118^{\circ}$ . The nitro-acid crystallises in long yellow needles soluble in ether and acetic acid. On reduction with tin and hydrochloric acid, the hydrochloride of metamidohydrocinnamic acid is obtained in flat colourless needles. The free base (m. p.  $84^{\circ}$ ) is soluble in acids, alkalis, alcohol, ether, and water.

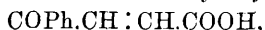
The following table shows the melting points of the nitro- and amido-hydrocinnamic acids:—

	Para.	Meta.	Ortho.
Nitrohydrocinnamic acid..	$163^{\circ}$	$118^{\circ}$	$113^{\circ}$
Amidohydrocinnamic acid	131	84	decomposes into water and hydrocarbostyrl.

W. C. W.

**Monochlorocinnamic Acid.** By G. W. JUTZ (*Ber.*, **15**, 788).—By treating phenyldichloropropionic acid (*Ber.*, **14**, 1867) with alcoholic potash, two potassium chlorocinnamates are obtained, which are separated by their different solubilities in alcohol. From the more soluble salt, a monochlorocinnamic acid may be obtained, crystallising in leaflets melting at  $114^{\circ}$ , whilst the other salt yields an acid crystallising in long needles melting at  $142$ — $143^{\circ}$ . P. P. B.

**Condensation-products of Bibasic Fatty Acids.** By H. v. PECHMANN (*Ber.*, **15**, 881—892).—*Benzoylacrylic acid*,



prepared by the action of aluminium chloride on benzene and maleic anhydride, is deposited from benzene in plates, and from toluene in long needles melting at  $99^\circ$ , sparingly soluble in cold water and light petroleum. The hot aqueous solution deposits white plates (m. p.  $64^\circ$ ), which contain water of crystallisation. This acid resists the action of dilute acids, but is decomposed by alkalis and alkaline carbonates, forming acetophenone and glyoxylic acid. When benzoylacrylic acid is boiled with twice its weight of acetic anhydride in a flask fitted with an upright condenser, ruby-red crystalline needles are deposited, which have the composition  $\text{C}_{10}\text{H}_8\text{O}_2$ . Boiling xylene is the menstruum best adapted for the recrystallisation of this substance. The crystals dissolve in cold sulphuric acid, forming a blue solution, which on the addition of water yields a red precipitate of the original substance. If the solution in strong sulphuric acid is gently heated, its colour changes to red, and on dilution with water a red solution, exhibiting an intense green fluorescence, is obtained. On distillation with a very small quantity of zinc-dust, a yellow crystalline compound is produced, which begins to sublime at  $290^\circ$ , and melts above  $500^\circ$ . It is soluble in benzene and xylene, forming brown solutions, which exhibit a green fluorescence. Benzoylacrylic acid unites with bromine, forming a colourless addition-product melting at  $135^\circ$ .

*Toluylacrylic acid*,  $\text{C}_6\text{H}_4\text{Me.CO.CH:CH.COOH}$  (m. p.  $138^\circ$ ), resembles benzoylacrylic acid in its properties, and yields a red condensation-product when treated with acetic anhydride.

*Benzoylpropionic acid*, described by Bureker (*Bull. Soc. Chim.*, **35**, 17), does not yield a condensation-product when boiled with acetic anhydride. On reduction with zinc-dust and acetic acid, a crystalline compound (m. p.  $165^\circ$ ) is obtained, which is soluble in alcohol, but insoluble in alkalis. On reduction with sodium amalgam, phenylhydroxybutyric acid,  $\text{OH.CHPh.}(\text{CH}_2)_2\text{COOH}$ , is produced. This acid melts at  $30^\circ$ , and decomposes on distillation, yielding phenylbutyrolactone (which has also been obtained from isophenylcrotonic acid by Fittig, *Annalen*, **208**, 121). The lactone melts at  $34^\circ$ . It dissolves freely in alcohol, ether, benzene, and acetic acid. From the sulphuric acid solution, water throws down a colourless precipitate, which possesses the properties of an acid.

*Benzoylcrotonic acid*,  $\text{COPh.CMe:CH.COOH}$ , prepared by the action of aluminium chloride on a mixture of benzene and citraconic anhydride, crystallises in needles melting at  $113^\circ$ . By boiling with alkalis, it is decomposed into propiophenone and glyoxylic acid, which are afterwards converted into glycolic and oxalic acids.

W. C. W.

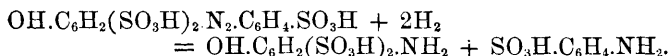
**Sulphonic Acids of Hydroxyazobenzene.** By H. LIMPRICHT (*Ber.*, **15**, 1295—1299).—By the action of warm fuming sulphuric acid azoxybenzene, four sulphonic acids of hydroxyazobenzene are formed, the monoacid by heating one part azoxybenzene with 5 parts sulphuric acid, the di-, tri-, and tetra-sulphonic acids by heating one part azoxy-

benzene with ten parts of acid. In order to separate the acids, the crude product is allowed to cool, whereby crystals of the monosulphonic acid separate out : the filtrate is then neutralised with lime, the calcium sulphate removed, and potassium carbonate added. The potassium salts of the three acids may be separated by fractional crystallisation from water.

*Hydroxyazobenzenemonosulphonic acid*,  $\text{SO}_3\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , crystallises in reddish leaflets, soluble in water, sparingly soluble in dilute acids. The potassium, barium, and silver salts also form similar crystals; the chloride (m. p.  $122^\circ$ ) crystallises in golden, the amide (m. p.  $212^\circ$ ) in flesh-coloured leaflets. The author was unable to establish the identity of this acid with previously prepared acids of similar constitution; it shows, however, some points of resemblance with the acid obtained by Griess from phenol and the diazo-derivative of paramidobenzenesulphonic acid.

*Hydroxyazobenzenedisulphonic acid*,  $(\text{OH})\text{C}_6\text{H}_4\text{N}_2(\text{SO}_3\text{H})_2$ , crystallises in golden needles, easily soluble in water, sparingly soluble in acids. The potassium salt crystallises in needles, the barium and silver salts form dark-red crystalline precipitates.

*Hydroxyazobenzenetrisulphonic acid*,  $\text{OH} \cdot \text{C}_6\text{H}_2(\text{SO}_3\text{H})_2 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$ , crystallises in ruby-red deliquescent needles, sparingly soluble in dilute acids. The potassium salt forms golden-yellow needles; the barium, lead, and silver salts are dark-brown crystalline precipitates. The chloride forms a reddish crystalline powder melting at  $220^\circ$ ; the amide, golden, sparingly soluble leaflets. By the action of reducing agents, hydroxyazobenzenetrisulphonic acid is converted into *paramidobenzenesulphonic* and *amidophenoldisulphonic acid* thus:—



The latter crystallises in delicate white needles, soluble in water, sparingly soluble in alcohol. It gives a violet coloration with ferric chloride. The hydrogen potassium, and ammonium salts crystallise in red prisms; the normal red salt is a crystalline precipitate. By passing nitrous acid into water in which the hydrogen potassium salt is suspended, a *potassium salt of a diazo-acid* is obtained, of constitu-

tion  $(\text{SO}_3\text{K})_2\text{C}_6\text{H}_2 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{N}$ , which crystallises in golden needles, ex-

plodes slightly on heating, and on boiling with water forms a potassium salt of a *quinoldisulphonic acid*,  $\text{C}_6\text{H}_2(\text{OH})_2(\text{SO}_3\text{K})_2$ . A solution of this latter salt forms a violet coloration with ferric chloride, reduces silver solution, and gives with barium chloride and lead acetate sparingly soluble precipitates. Inasmuch as in hydroxyazobenzene the N and OH groupings are in the para-position, it follows that in the amidophenoldisulphonic acid the  $\text{NH}_2$  and OH groupings must be in the same position; further, as paramidobenzenesulphonic acid is formed by the reduction of the trisulphonic acid, the latter must have the constitution  $\text{C}_6\text{H}_2(\text{OH})(\text{SO}_3\text{H})_2 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$ ;  $\text{OH} : \text{N} = 1 : 4$ , and  $\text{SO}_3\text{H} : \text{N} = 1 : 4$ ; but the position of the two sulphonic groupings is uncertain.



*Hydroxyazobenzenetetrasulphonic acid*,  $C_{12}H_5OHN_2(SO_3H)_4$ , cannot be obtained in the crystalline state. Its potassium salt forms golden-yellow interlaced needles, its barium salt a crystalline precipitate. The solution of the potassium salt reduces silver solution, and forms a precipitate of tribromophenol with bromine-water. V. H. V.

**Preparation of Dextrorotatory Mandelic Acid from the Optically Inactive Acid.** By J. LEWKOWITSCH (*Ber.*, 15, 1505).—The author finds that solutions of inactive mandelic acid (ammonium salt) when sown with various microzoa, e.g., *Bacterium termo*, *Aspergillus*, *Mucor*, *Penicillium glaucum*, exhibit the phenomenon of gradual development of optical activity (dextrorotation). The explanation lies in the destruction by the organisms of the levorotatory acid, which is moreover that obtained by the action of hydrochloric acid on amygdalin, and therefore formed by the "natural" process. The observation is therefore in sequence with the various similar cases observed by Pasteur and by Le Bel (*Compt. rend.*, 46, 51, 87, 89, 92), and in harmony with the hypothesis that the optical inactivity of bodies prepared by artificial synthesis is due to the simultaneous formation of the antithetical isomerides. The author is pursuing the subject. C. F. C.

**Vulpic Acid.** By A. SPIEGEL (*Ber.*, 15, 1546—1554).—The author has investigated the bodies which accompany dihydrocornicularic acid, as products of reduction of pulvinic acid, and has thereby established both their mode of origin and the constitution of the parent substance, pulvinic acid. These products may be arranged in the following series, the corresponding lactones to which, like pulvic acid, they give rise being also formulated:—

		Lactone.
1. Pulvic acid.....	$C_{18}H_{12}O_5$	$C_{18}H_{10}O_4$
2. Carboxycornicularic acid ..	$C_{18}H_{14}O_5$	$C_{18}H_{12}O_4$
3. Cornicularic „ ..	$C_{17}H_{14}O_3$	$C_{17}H_{12}O_2$
4. Dihydrocornicularic „ ..	$C_{17}H_{16}O_3$	$C_{17}H_{14}O_2$
5. Isodihydrocornicularic „ ..		
6. Tetrahydrocornicularic „ ..	$C_{17}H_{18}O_3$	$C_{17}H_{16}O_2$
7. Diphenylvaleric „ ..	$C_{17}H_{18}O_2$	—

Of these, 4 constitutes the crystalline portion of the product of the reduction of pulvic acid with zinc-dust in presence of ammonia, 2, 3, 5, and probably also 6 occurring in the non-crystalline portion (*ibid.*, 14, 1686): this portion was treated with acetic anhydride, and the resulting crystalline anhydrides were separated by recrystallisation from alcohol, from a non-crystalline residue. This paper being anticipatory of a fuller publication, the following particulars of the research are given in bare outline.

*Lactone of carboxycornicularic acid*,  $C_{18}H_{12}O_4$ , crystallises from alcohol in short prisms, and from benzene in long needles (m. p.  $215^\circ$ ). With ammonia and alkaline carbonates, it forms salts,  $C_{18}H_{11}O_4M$ , which are of a yellow colour, and but slightly soluble in cold menstrua. The attempt to resolve the lactone group by the application of heat and thus obtain salts of the formula  $C_{18}H_{12}O_5M_2$ ,

results in the simultaneous removal of  $\text{CO}_2$  and the formation of colourless salts of cornicularic acid.

The *lactone of cornicularic acid*,  $\text{C}_{17}\text{H}_{12}\text{O}_3$ , crystallises from its alcoholic solution in yellow needles melting at  $141^\circ$ . It is not dissolved by aqueous alkalis on heating, but on warming its alcoholic solution with a little aqueous alkali, it is converted into cornicularic acid.

*Cornicularic acid*,  $\text{C}_{17}\text{H}_{14}\text{O}_3$ , is separated from the solution resulting from the two preceding decompositions, in oily drops which solidify to long colourless needles melting at  $115^\circ$ . By heat, it is converted into the corresponding lactone, and when treated with acetic anhydride, it yields a non-crystalline oily mass, which is insoluble in alkalis, and is probably an addition product of the lactone, and contained in the mixture of products of reduction of pulvinic acid, after similar treatment. On heating it with aqueous soda and zinc-dust, the acid is converted into dihydrocornicularic acid.

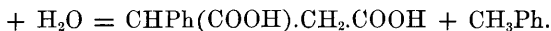
The *lactone of isodihydrocornicularic acid*,  $\text{C}_{17}\text{H}_{14}\text{O}_2$ , crystallises from alcohol in colourless needles melting at  $104^\circ$ . Dihydro- and tetrahydro-cornicularic acid have been previously described.

*Diphenylvaleric acid* is connected with the previous acid, which has been shown by the author to be diphenyloxyvaleric acid. Its reduction to diphenylvaleric acid takes place with difficulty, requiring the employment of phosphorus and hydriodic acid.

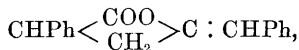
*Constitution of the Reduction-products.* (a.) *Dihydrocornicularic Acid*,  $\text{C}_{17}\text{H}_{16}\text{O}_3$ .—Of the reduction products of pulvinic acid, dihydrocornicularic acid is the most important, from the fact of undergoing a simple decomposition, which throws great light upon its constitution. Its decomposition on heating it with aqueous potash into phenyl-succinic acid and toluene is most easily explained by regarding it as phenylsuccinic acid, in which substitution has taken place in that carboxyl-group most remote from the phenyl residue, and in such a way that either an oxygen-atom has given place to the diatomic benzal residue or hydroxyl to the monatomic benzyl residue. The two views may be formulated as under:—

- (1.)  $\text{CHPh}(\text{COOH})\cdot\text{CH}_2\cdot\text{C}(\text{OH}) : \text{CHPh}.$
- (2.)  $\text{CHPh}(\text{COOH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\text{Ph}.$

and the resolution of the acid by the equation—



The first formula is apparently confirmed by the fact that dihydrocornicularic acid is converted on heating into a lactone,  $\text{C}_{17}\text{H}_{14}\text{O}_2$ , which must have the following constitutional formula:—



but cannot be reconciled with Erlenmeyer's conclusion (*ibid.*, **13**, 309)

that all tertiary alcohols, in which two affinities of the radicle  $\text{COH}$  are satisfied by two of a carbon-atom, must be resolved into a ketone, and according to which dihydrocornicularic acid could only possess at the moment of its formation the constitution expressed in the first

formula. The methyl ether of the acid moreover resists the action of acetic anhydride at  $180^{\circ}$ , and cannot therefore contain an OH-group. The second of the above formulæ is that which must be retained, the formation of the lactone being characterised by the passage of the  $-\text{CO}.\text{CH}_2\text{-group}$  into  $-\text{C}(\text{OH}) : \text{CH}-$ . This view is supported by the fact that dihydrocornicularic acid is resolved on distillation with lime into carbonic anhydride, and a diphenyl-methyl-ethyl ketone,

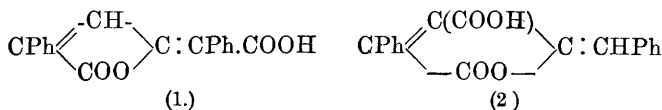


This ketone corresponds in its properties with that obtained by the author in the distillation of a mixture of the calcium salts of hydrocinnamic and phenylacetic acids.

(b.) *Cornicularic acid*,  $\text{C}_{17}\text{H}_{14}\text{O}_3$  is converted into its dihydro-derivative in such a way as to leave no doubt that its constitution is that expressed by the formula:  $\text{CPh}(\text{COOH}) : \text{CH}.\text{CO}.\text{CH}_2\text{Ph}$ , i.e., it is related to phenylfumaric acid in the same way as its hydrogen addition-product is to phenylsuccinic acid. The constitution of its lactone

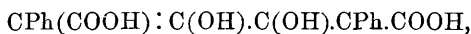
is expressed by the formula:  $\text{CPh} \begin{array}{c} \text{COO} \\ \diagup \quad \diagdown \\ \text{CH} \end{array} \text{C} : \text{CHPh}.$

(c.) *Lactone of carboxycornicularic acid*,  $\text{C}_{18}\text{H}_{12}\text{O}_4$ , contains a  $\text{COOH}$ -group additional to the last named, and may be represented hypothetically by the two possible constitutional formulæ:—



Of these (1) is more probably the correct one, and for the following reasons. The acid is obtained from pulvic acid by a reduction which cannot be regarded as affecting the union of the carboxyl-groups. Pulvic acid further is resolved by the action of baryta-water into 2 mols. phenylacetic acid, and 1 mol. oxalic, and its 2  $\text{COOH}$ -groups are therefore in union with the C-atoms nearest the Ph residues. Carboxycornicularic acid,  $\text{C}_{18}\text{H}_{14}\text{O}_5 = \text{CPh}(\text{COOH}) : \text{CH}.\text{COCHPh}.\text{COOH}$ , must exist among the non-crystalline products of reduction of pulvic acid, from which its lactone was obtained.

*Constitution of Pulvic and Vulpic Acids.*—Pulvic acid differs from the last-named acid by containing 2 H atoms less, and its derivation therefore must be assumed to take place by way of a hypothetical hydrate, which loses water to form pulvic acid, thus:—

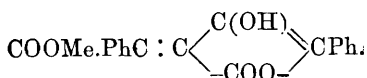


becoming  $\text{COOH}.\text{CPh} : \text{C} \begin{array}{c} \text{C}(\text{OH}) \\ \diagup \quad \diagdown \\ \text{COO} \end{array} \text{CPh}.$

The constitution of pulvic anhydride as derived from this formula would be that of a diphenyl diacetylene  $\text{CPh} \equiv \text{C}-\text{C} \equiv \text{CPh}$ , combined with two  $\text{CO}_2$  groups to form a double lactone, and this is in harmony with the fact that it is insoluble in alkalis and yields no diacetyl-

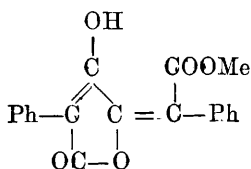
derivative. Baeyer having set out from this hydrocarbon in his synthesis of indigo, the pulvinic series derive additional interest from their relationship to this body.

*Ethers of Pulvic Acid.*—Pulvic acid being dibasic yields two series of salts. Vulpic acid is the methyl ether, and has the following constitution:—

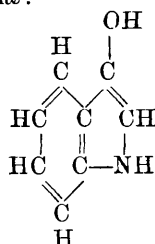


The combination of the OH-group with a tertiary C-atom harmonises with the ready conversion of the acid into an acetyl-derivative, together with loss of its acid character. The existence of an isovulpic acid also argues for the presence in pulvic acid of two OH-groups of different function. Vulpic acid is monobasic and yields dimethyl vulvate, identical with that obtained from the neutral silver salt of pulvic acid.

The phenol-character of the OH-group in vulpic acid is conditioned by its connection with a closed chain, analogously to indoxyl, as is seen from the following comparative formulæ:—



Vulpic acid.



Indoxyl.

C. F. C.

**Researches on Usnic Acid and other Substances extracted from Lichens.** By E. PATERNÒ (*Gazzetta*, 1882, 231—261).—

I. USNIC ACID AND ITS DERIVATIVES.—In a paper published some years ago (*Gazzetta*, 1876, 113; Abstr., *C. J.*, 1876), the author assigned to usnic acid the formula  $\text{C}_{18}\text{H}_{16}\text{O}_7$ , and stated that when heated at  $150^\circ$  in sealed tubes with alcohol, it underwent a decomposition represented by the equation  $\text{C}_{18}\text{H}_{16}\text{O}_7 + 2\text{H}_2\text{O} = \text{CO}_2 + \text{C}_2\text{H}_4\text{O}_2 + \text{C}_{15}\text{H}_{16}\text{O}_5$  (decarbusnic acid), and that when heated with potash in a stream of hydrogen, it yielded pyrousnic acid,  $\text{C}_{12}\text{H}_{12}\text{O}_3$ , according to the equation  $\text{C}_{18}\text{H}_{16}\text{O}_7 + 3\text{H}_2\text{O} = \text{C}_3\text{H}_6\text{O} + \text{CO}_2 + \text{C}_2\text{H}_4\text{O}_2 + \text{C}_{12}\text{H}_{12}\text{O}_3$ ; further, that this last acid, when heated, easily gave off  $\text{CO}_2$ , being converted into a new body, probably  $\text{C}_{11}\text{H}_{12}\text{O}_3$ , and that by slightly varying the conditions of the action of potash on usnic acid, a new body allied to pyrousnic acid might be obtained.

II. Salkowski, on the other hand (*Ber.*, 8, 1460; Abstr., 1876, 599), represented usnic acid by the formula  $\text{C}_{18}\text{H}_{18}\text{O}_7$ , and supposed that when fused with potash, it yielded an acid,  $\text{C}_9\text{H}_{10}\text{O}_4$ , according to the equation  $\text{C}_{18}\text{H}_{18}\text{O}_7 + \text{H}_2\text{O} = 2\text{C}_9\text{H}_{10}\text{O}_4$ . He afterwards endeavoured to account for the difference between his own results and those of Paternò by supposing that the experiments of the latter were made

with the true usnic acid, whereas he himself had operated on Hesse's carbusnic acid,  $C_{18}H_{18}O_8$ . To this Paternò replied (*Gazzetta*, 1878, 225, Abstr., 1878, 882) that these supposed two acids are really identical, and that if the composition of the potassium salt does not appear consistent with his own formula,  $C_{18}H_{16}O_7$ , the difference may be ascribed to the fact that the so-called usnic acid is really an anhydride, and that the salts of the corresponding acid have the composition  $C_{18}H_{17}MO_8$ . These conclusions have not been contradicted either by Salkowski or by Hesse, and appear indeed to have received general assent. Stenhouse and Groves, however (this *Journal*, Trans., 1881, 234), by heating usnic acid with sulphuric acid, have obtained an acid which they call *usnic acid*, and represent by the formula  $C_{27}H_{24}O_{10}$ , whence they deduce for usnic acid the formula  $C_{54}H_{50}O_{21}$ . The existence of another acid called *β-usnic* or *cludonic acid*, had previously been indicated by Hesse and corroborated by Stenhouse, who moreover regarded his *β-orcinol* as a product of transformation of that acid. Paternò, on the other hand, infers from his own experiments, that *β-usnic acid* is not a distinct compound, but merely usnic acid, the melting point of which has been lowered by admixture with other substances. It has since indeed been shown by Stenhouse and Groves (*Annalen*, 203, 285) that the true source of *β-orcinol* is a well-defined acid, which they call *barbatic acid*.

All these facts seem to indicate that the usnic acid with which the several experiments above alluded to were made, must have been more or less impure.

Paternò, in continuing his experiments, has arrived at the following results:—

1. *Decarbusnein*, to which he formerly assigned the formula  $C_{15}H_{17}O_5$ , representing its formation by the equation  $C_{18}H_{16}O_7 + 2H_2O = CO_2 + C_2H_4O_2 + C_{15}H_{16}O_5$  (the presence of acetic acid having been inferred merely from its odour), he now finds to have the composition  $C_{17}H_{18}O_6$ , and to be produced by the reaction  $C_{18}H_{16}O_7 + H_2O = CO_2 + C_{17}H_{18}O_6$ . It is prepared by heating usnic acid with alcohol in sealed tubes at  $150^\circ$ . It exhibits some of the characters of an acid, dissolving readily in alkalis, but it is extremely oxidisable, and does not easily form definite salts. Its ammoniacal solution reduces silver nitrate, and its alkaline solutions quickly absorb oxygen. By heating with potash, it is converted into an acid having the formula  $C_{15}H_{16}O_5$ , formerly assigned to decarbusnein itself.

2. *Decarbusnic acid*,  $C_{15}H_{16}O_5$ , is formed by boiling decarbusnein with potash in a flask filled with hydrogen, and is precipitated from the resulting solution by hydrochloric acid as a yellow powder. It dissolves in alcohol, and crystallises therefrom in short heavy yellow prisms, melting at  $198$ – $199^\circ$ . It is moderately soluble in boiling alcohol, very slightly in cold alcohol and in ether, and apparently insoluble in water. Heated for four hours in a reflux apparatus with acetic anhydride, it yields two substances separable by repeated crystallisation from alcohol and ether, the one first deposited melting at  $147$ – $148^\circ$ , the other at  $130$ – $131^\circ$ . These bodies are acetyl-derivatives of decarbusnic acid, represented by the formulæ  $C_{15}H_{15}AcO_5$  and  $C_{15}H_{14}Ac_2O_5$ , the former being isomeric with decarbusnein. In the

action of potash on decarbusnein there is also formed a small quantity of pyrousnetic acid.

3. *Pyrousnetic acid*,  $C_{14}H_{14}O_6$ , is prepared by heating usnic acid with aqueous potash (10 pts. usnic acid, 25 KOH, and 25 water) over the water-bath for about half an hour (at higher temperatures over an open fire pyrousnetic acid is formed), and is precipitated from the resulting solution by hydrochloric acid in yellow flocks. When purified by crystallisation from boiling alcohol and washing with ether, it forms laminæ or flattened needles, having a light greyish-yellow colour and pearly lustre. It melts at  $183-186^\circ$  with blackening and decomposition. It is slightly soluble in water, easily in boiling alcohol, sparingly in cold alcohol, moderately in ether and in benzene. Heated with water at  $130-140^\circ$  in sealed tubes for about four hours, it dissolves completely, and separates on cooling, without alteration, in small light yellow prisms melting at  $185^\circ$ . The formation of pyrousnetic acid by the action of potash on usnic acid might be represented by either of the equations:  $C_{18}H_{16}O_7 + 2H_2O = C_{14}H_{14}O_6 + C_3H_6O + CO_2$ , or  $C_{18}H_{16}O_7 + 3H_2O = C_{14}H_{14}O_6 + 2C_2H_4O_2$ , the former of which appears to be the more probable, the formation of acetone being actually observed.

Pyrousnetic acid is converted by the action of acetic chloride at the heat of the water-bath, into a *monacetyl-derivative*,  $C_{14}H_{13}AC_2O_6$ , which crystallises from acetic acid or aqueous alcohol in small greyish-white needles, very soluble in alcohol and in benzene, slightly in ether, still less in water. It melts at  $168^\circ$ , does not lose weight by drying at  $100^\circ$ , but undergoes considerable alteration at  $120^\circ$ ; and on crystallising the modified product from aqueous alcohol, a small portion of the original substance separates out, while pyrousnetic acid remains in the mother-liquors. The acetyl-derivative dissolves in cold concentrated aqueous potash, forming a solution from which hydrochloric throws down pyrousnetic acid; and if the action be aided by heat, an odour of acetone is given off, the alkaline solution turns green (from the action of atmospheric oxygen), and hydrochloric acid then gives only a slight precipitate. These changes probably indicate the formation of pyrousnetic acid.

4. *Usnetol*,  $C_{13}H_{14}O_4$ , is formed, together with carbonic anhydride, by heating pyrousnetic acid at  $185^\circ$  in a stream of hydrogen:  $C_{14}H_{14}O_6 = CO_2 + C_{13}H_{14}O_4$ , and crystallises from aqueous alcohol in very beautiful long shining yellowish needles; from benzene in smaller needles; melts at  $179^\circ$ .

5. *Pyrousnic acid*,  $C_{12}H_{12}O_5$ , prepared, as already described by the author (*Gazzetta*, 1876, 113; *Chem. Soc. J.*, 1876, [ii], 202), is converted by boiling with excess of acetic chloride, into an acetyl-derivative which crystallises in prisms often forming radiate groups, having a silky lustre when large and isolated. They have a faint rosy tint like that of manganous salts, melt at  $205^\circ$ , and dissolve in alcohol, ether, benzene, acetic acid, aqueous alcohol, and boiling water, without alteration even at boiling heat. The composition of this acetyl-derivative has not been completely made out, but the analyses agree best with the formula of a diacetyl-compound. It is not altered by heating with water up to  $120^\circ$ , but at higher temperatures acetic acid is formed, together with a brown oily substance.

6. *Usneol*,  $C_{11}H_{12}O_3$ , is formed by the dry distillation of pyrousnic acid in a current of hydrogen:  $C_{12}H_{12}O_5 = CO_2 + C_{11}H_{12}O_3$ . When purified by repeated crystallisation from aqueous alcohol, or from ether or benzene, it forms radial groups of small white prisms, having a pearly lustre when crystallised from benzene. When pure, it melts at  $175^\circ$ . It is very soluble in alcohol and ether, only slightly in chloroform and commercial benzene, still less in cold water; more soluble in pure benzene. The aqueous solution reduces silver nitrate, and gives a dirty white precipitate with ferric chloride.

Usneol dissolves in acetic chloride at the boiling heat, and on distilling off the excess of the latter after several hours' heating, there remains a brown oily substance, which gradually solidifies to a blackish crystalline mass; and on removing the brown substance by washing with ether and repeatedly crystallising the residue from aqueous alcohol, ether, and acetic acid, white needles are obtained melting at  $141$ – $142^\circ$ , volatile without decomposition, and giving by analysis numbers approaching nearly to the composition of a diacetyl derivative,  $C_{11}H_{10}Ac_2O_3$ . It is remarkable that, whereas the acetyl-derivatives of carbusnic acid, pyrousnetic acid and usnetol, have melting points lower than those of the compounds from which they are derived, the acetyl-derivative of pyrousnic acid melts at a higher temperature than pyrousnic acid itself. Usneol fused with potassium hydroxide yields a substance analogous to catechol.

7. *Usnolic Acid*.—This name was given by Stenhouse and Groves, as already stated, to a derivative of usnic acid, to which they assign the formula  $C_{27}H_{24}O_{10}$ , founded on the mean results of their analyses, viz., 63.78 per cent. carbon and 5.02 hydrogen. As, however, this formula has no obvious relation to that of usnic acid, or to those of any of its derivatives above described, the author was induced to re-examine the composition of the acid, which he prepared exactly in the manner described by Stenhouse and Groves. In five analyses he obtained 62.27 to 62.90 per cent. carbon, and 4.87 to 5.13 hydrogen, but he has not attempted to deduce a formula therefrom.

8. *Usnic Anilide*,  $C_{24}H_{21}O_6N = NH_2(C_{24}H_{19}O_6)$ .—This compound is prepared by gently heating usnic acid dissolved in benzene or suspended in alcohol, with excess of aniline, and crystallising the product from boiling alcohol or from acetic acid; also by heating an alcoholic solution of potassium usnate with aniline hydrochloride. It crystallises from boiling alcohol in thin laminæ having a pale lemon-yellow colour and vitreous lustre, and from acetic acid in hard heavy prisms. It melts at  $170$ – $171^\circ$ ; is moderately soluble in boiling, very sparingly in cold alcohol; sparingly also in ether, very freely in hot acetic acid and in benzene.

Usnic anilide dissolves readily in cold aqueous potash, forming a yellow solution from which hydrochloric acid throws down a substance having the appearance and melting point ( $169$ – $171^\circ$ ) of the anilide itself, but differing therefrom in composition, its analysis leading to the formula  $C_{23}H_{23}O_6N$ , analogous to that of decarbusnein. The anilide is not altered in any way by boiling with dilute hydrochloric or sulphuric acid, but dissolves in strong sulphuric acid, yielding a red solution from which water throws down yellow flocks of a new

substance still containing the aniline residue. The anilide likewise remains unaltered when boiled with acetic chloride, but when heated in sealed tubes at  $120^{\circ}$  with acetic anhydride, it partly decomposes, apparently however without formation of acetyl-derivatives. At  $160^{\circ}$  in sealed tubes, it is converted into a substance crystallising from boiling alcohol in very slender needles, which begin to become coloured at  $200^{\circ}$ , scarcely soften at  $220^{\circ}$ , but decompose at a higher temperature, giving off aniline, together with other volatile products.

II. FISCIC ACID.—This name is given by the author to a new acid, extracted by himself and Seichilone from *Fiscia parietina*, a lichen growing abundantly in Sicily on the branches of shrubs. It is prepared by exhausting the lichen in a percolator with boiling alcohol, whereby a black viscous mass is obtained; and on treating this with ether, the new acid remains undissolved in the form of a nearly black powder, which may be purified by washing with ether, and crystallising several times from benzene, in presence of animal charcoal. The yield is very small.

Fiscic acid forms red-brown crystals, which melt at  $204\text{--}204.5^{\circ}$ , and dissolve readily in potassium hydroxide and carbonate, forming red salts like those of chrysophanic acid. When reprecipitated from the potash-solution, and crystallised from alcohol, it loses its red colour and crystallises in canary-yellow needles melting at  $200^{\circ}$ , apparently identical however with the original substance. It exhibits considerable resemblance to chrysophanic acid, but is distinguished from the latter by its composition and higher melting point. Heated with acetic anhydride, it forms an acetyl-derivative, and when distilled with zinc-dust, it yields a solid hydrocarbon different from anthracene and methylantracene, but not yet satisfactorily examined.

The greater part of the alcoholic extract of *Fiscia parietina* consists of a brown viscid substance, which when heated with potash, gives off a very volatile base having a strong alkaline reaction and ammoniacal odour.

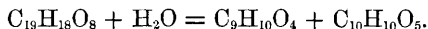
III. ATRANORIC ACID AND ITS DERIVATIVES. *Rangiformic Acid*.—Atranoric acid originally found in *Lecanora atra*, and afterwards in *Stearocaulon vesuvianum* (*Gazzetta*, 1878, 289), has lately been obtained by the author from *Cladonia rangiformis*, which grows abundantly in thickets near Palermo. It is extracted by ether, together with usnic acid, from *Lecanora atra*; and is accompanied in *Cladonia rangiformis* by a new acid called by the author rangiformic acid.

*Cladonia rangiformis*, well dried in the sun and pulverised, gives up to ether about a third of its weight of a nearly white or slightly yellow crystalline product, from which the atranoric acid may be obtained by first treating it with boiling alcohol and with ether, which remove the rangiformic acid, and crystallising the undissolved residue from chloroform, from benzene, or better from boiling xylene. Atranoric acid thus prepared melts, like that obtained from the other lichens above mentioned, at  $190\text{--}194^{\circ}$ , according to the purity of the specimen; it



is very slightly soluble in cold alcohol, ether, chloroform or benzene, moderately soluble in boiling chloroform and benzene, more freely in hot xylene. Potash and ammonia dissolve it readily, forming canary-yellow solutions, from which it separates unaltered on addition of hydrochloric acid. Its analysis gave 60.60 to 61.19 per cent. C and 4.92 to 5.19 H, leading to the formula  $C_{19}H_{18}O_8$ , which requires 60.96 C and 4.81 H.

*Atranorinic acid*,  $C_9H_{10}O_4$ , and *Atraric acid*,  $C_{10}H_{10}O_5$ , are formed, with evolution of carbonic anhydride, when atranoric acid is heated with water in sealed tubes at  $150^\circ$ . The former, which is much the more soluble in boiling water of the two, crystallises in the tubes in splendid needles; the latter, which is much less soluble, separates in the form of a brown resinous mass. Atranorinic acid purified by repeated crystallisation from boiling water melts at  $100-101^\circ$ ; it is much less soluble in cold than in boiling water, moderately soluble in alcohol and in ether, easily soluble in alkalis and alkaline carbonates, forming yellow solutions. With silver nitrate its ammoniacal solution gives a greenish precipitate which alters rapidly on exposure to light. Its aqueous solution is coloured brownish-green by ferric chloride, blood-red by calcium chloride. *Atraric acid*, purified by crystallisation from alcohol in presence of animal charcoal, crystallises in micaceous laminæ, melting at  $140-141^\circ$ , only slightly soluble in water even at the boiling heat, freely soluble in alcohol and in ether. It dissolves readily also, without coloration, in alkalis and alkaline carbonates; its silver salt quickly turns brown on exposure to light. With calcium chloride, it reacts like atranoric and atranorinic acid, but gives no reaction with ferric chloride. The formation of these two acids from atranoric acid is represented by the equation:



The evolution of carbonic anhydride appears to be due to a secondary action.

*Rangiformic acid* is contained in *Cladonia rangiferina*, together with atranoric acid, from which it may be separated by its greater solubility in alcohol. By crystallisation from boiling benzene, it is obtained in white laminæ melting at  $104-106^\circ$ . It gave by analysis 65.13 per cent. C and 9.84 H, agreeing approximately with the formula  $C_{11}H_{18}O_3$ , which requires 66.66 C and 9.09 H. It may therefore be regarded as a lower homologue of Schredermann and Knop's lichenstearic acid,  $C_{14}H_{24}O_3$ . It dissolves readily in ammonia, and silver nitrate added to the solution throws down white flocks of silver rangiformate. Further details respecting this acid are promised in a future communication.

H. W.

**Formation and Decomposition of Acetanilide.** By N. MENSCHUTKIN (*Journ. Russ. Chem. Soc.*, 1882, 260-277).—The author refers to his previous papers on the etherification of alcohols and acids, and proceeds to investigate the question, how far the same phenomena as in the above case are repeated with compounds which are not ethereal salts? Such compounds are amides of acids. But as the investigation of amides offers some experimental difficulties, the author has hitherto examined only substituted amides. He has

selected for his experiments acetanilide, the formation of which takes place according to the following equation:  $\text{PhH}_2\text{N} + \text{AcHO} = \text{AcPhHN} + \text{H}_2\text{O}$ . In order to study this reaction as fully as possible, the author has applied an experimental method strictly analogous to that employed by him in his previous researches on etherification. Weighed quantities of aniline and acetic acid were sealed in glass tubes, and after being heated for a definite length of time and to different temperatures, the quantities of the substances which entered into reaction were calculated from the amount of acetic acid which remained after the reaction in the form of aniline acetate. The quantity of acetic acid was determined volumetrically by baryta added until the neutral reaction was restored, as, according to the author's experiments, baryta completely decomposes aniline acetate, which, like all salts of aniline, shows an acid reaction. The results obtained by the author are contained in four sections:—

(1.) *Velocity of Formation of Acetanilide and the Influence of Temperature on its Formation.*—The experiments were carried on with molecular quantities of acetic acid and aniline. The following numbers give the velocity and limit of *amidation* (formation of the amide, a term analogous to etherification) in the above mixture at  $155^\circ$ :—

Coefficient.	1 hr.	2 hrs.	4 hrs.	8 hrs.	12 hrs.	24 hrs.
0.3921	58.28	65.86	73.61	77.30	78.12	79.17
	48 hrs.	120 hrs.	168 hrs.	240 hrs.		
	79.77	79.68	79.97	79.52		

The *initial velocity* of “amidation” (during the first hour) = 58.28 per cent. is very great, and the limit is reached in 24 hours.

The distribution of the velocity is seen from the following numbers:—

	Absolute velocity. Per cent. in 1 hour.
During the 1st hour .....	58.28
„ 2nd „ .....	7.58
„ 3rd and 4th hour .....	3.87
From 4 to 8 hours .....	0.92
„ 8 to 12 „ .....	0.20

The *relative initial velocity*, the limit 79.68 being taken as 100, is = 73.14, a number which is larger than the absolute velocity. It decreases rapidly, being after the first hour = 9.51, after the second hour = 4.86, and so on. As the initial velocity is very great, and as during the first hour no acetanilide is decomposed by the action of water, the author has most carefully investigated the formation of acetanilide during the first hour. The mixture was sealed in a small and thin glass tube, then dipped into the bath for a definite number of minutes and afterwards cooled quickly. The time was determined by means of a “secondimeter” and the error committed was not above half a second. The following results were obtained:—

1 min.	2 min.	3 min.	4 min.	5 min.	10 min.
1.80	5.03	7.86	9.50	12.30	25.30
1.89	4.68	7.69	10.78	—	25.42
	15 min.	30 min.	45 min.	1 hour.	
	34.86	48.18	51.10	58.28	
	34.57	47.23	52.42	(mean)	

The *distribution of velocity* of the formation of acetanilide during the first hour is given by the following numbers :—

					Absolute velocity.
During the 1st minute.....					1.84 per cent.
„	2nd	„	.....		3.01 „
„	3rd	„	.....		2.92 „
„	4th	„	.....		2.37 „
„	5th	„	.....		2.16 „
From 5 to 10 minutes .....					2.16 in one minute.
„	10	„	15	„	1.88 „ „
„	15	„	30	„	0.86 „ „
„	30	„	45	„	0.27 „ „
„	45	„	60	„	0.43 „ „

The velocity diminishes rapidly with increasing time, but as the maximum falls within the 2nd minute, it seems that a kind of *inertia* must be overcome before the reaction is fully established. The following numbers were found at a temperature of 125° :—

Coefficient.	15 min.	30 min.	1 hr.	2 hrs.	12 hrs.
0.3921	12.27	22.58	33.19	49.89	73.51
	24 hrs.	168 hrs.	216 hrs.	240 hrs.	
	79.00	82.99	82.23	83.13	

The velocity reaches a maximum during the first hour, and shows a distribution analogous to that in the above cases. The same is seen from the following numbers expressing the formation of the amide at 100° :—

Coeff.	1 hr.	2 hrs.	4 hrs.	8 hrs.	12 hrs.	24 hrs.	36 hrs.	48 hrs.
0.3921	14.25	23.62	34.67	49.32	54.97	66.62	71.27	74.32
	72 hrs.	96 hrs.	144 hrs.	240 hrs.	312 hrs.	384 hrs.	456 hrs.	
	78.43	80.81	82.48	{ 85.07 84.20 }	84.93	84.91	85.31	

Finally, at the ordinary temperature, the following numbers were found :—

Days.	2.	5.	12.	31.	59.	139.
Percentage of "amidation" ..	1.13	5.44	8.22	12.22	25.54	43.77

As regards the influence of temperature on the formation of acetanilide, the author shows that it begins to take place at the ordinary temperature, as aniline acetate cannot exist even under those condi-

tions without being decomposed, and further, that the quantity of acetanilide formed by the "amidation" increases with increasing temperature. The same quantity of acetanilide (about 13 per cent.) requires for its formation the following length of time at different temperatures :—

Temperature.	Time.	Percentage of "amidation."
Ordinary.....	31 days (= 9000)	12·22
100°.....	1 hour (= 12)	14·25
125 .....	15 mins. (= 3)	12·27
155 .....	5 „ (= 1)	12·30

The following quantities of acetanilide require the *same length of time* for their formation :—

Temperature.	Initial velocity.
100°	14·25
125	33·19
155	58·28

For shorter intervals :—

Temperature.	30 min.	15 min.
125°	22·61	12·27
155	47·70	34·71

On comparing the formation of acetanilide with that of the ethyl or phenyl acetate, the author shows that the former takes place far more quickly.

(2.) *Existence of a Limit in the Formation of Acetanilide, and the Relation between the Limit and the Temperature.*—Simultaneously with the formation of acetanilide from acetic acid and aniline, its decomposition by water takes place, and after some time a limit is reached at which the two reactions are in a state of equilibrium. In addition to the above numbers the following numbers were found :—

Temp.	Coeff.	168 hrs.	216 hrs.	240 hrs.
135°	0·3921	82·30	82·25	82·65
145	0·3921	81·26	81·23	81·17

According to Berthelot and P. de St. Gilles, the limit of etherification in the formation of ethereal salts does not change with the temperature, and Menschutkin has shown that the temperature exerts the same influence on the velocity of the direct and the inverse reactions. In the case of acetanilide, this influence of temperature is unequal, and therefore the limit of its formation varies with the temperature, as is seen from the following numbers :—

Temperature.	Limits.
100°	85·05
125	83·11
135	82·39
145	81·22
155	79·68

A rise of temperature is more favourable to the decomposition of acetanilide by water than to its formation.

(3.) *The decomposition of Acetanilide by water* could be studied only in two cases, owing to the action of water on glass at high temperatures. In order to avoid such an action, a trace of free acetic acid was added. On heating acetanilide with water in molecular quantities at  $155^{\circ}$ , the following numbers were found:—

Time.	72 hrs.	192 hrs.
Acetanilide decomposed ....	19.75	19.57
Limit .....	80.25	80.34

Owing to the experiments being less accurate, the numbers differ a little from the limit 79.68 as found above.

(4.) *Influence of Mass on the Velocity of Formation of Acetanilide and on the Limit of that Reaction.*—(a.) 1 mol. of acetic acid was heated with varying quantities of aniline at  $155^{\circ}$ . The numbers indicate the percentage of acetic acid converted into acetanilide:—

Proportion.	Coeff.	15 min.	1 hr.	24 hrs.	Limit (216 hrs.).
$1\text{C}_6\text{H}_7\text{N} + 1\text{C}_2\text{H}_4\text{O}_2$ ..	0.3921	34.71	58.28	79.17	79.68
$2\text{C}_6\text{H}_7\text{N} + 1\text{C}_2\text{H}_4\text{O}_2$ ..	0.2439	28.71	$\left\{ \begin{array}{l} 57.92 \\ 58.00 \end{array} \right\}$	91.40	$\left\{ \begin{array}{l} 91.28 \\ 92.02 \end{array} \right\}$
$3\text{C}_6\text{H}_7\text{N} + 1\text{C}_2\text{H}_4\text{O}_2$ ..	0.1769	23.45	57.59	94.18	94.61
$4\text{C}_6\text{H}_7\text{N} + 1\text{C}_2\text{H}_4\text{O}_2$ ..	0.1412	—	52.43	92.53	96.17
$8\text{C}_6\text{H}_7\text{N} + 1\text{C}_2\text{H}_4\text{O}_2$ ..	0.0746	17.13	43.60	86.23	$\left\{ \begin{array}{l} 96.88 \\ 97.57 \end{array} \right\}$

As the quantity of aniline is increased, the limit increases at first rapidly and afterwards slowly, but the conversion is not complete, the highest percentage being 97.22. On the contrary the initial velocity diminishes with increase in the quantity of aniline; for this reason only in the first three cases is the limit reached in 24 hours.

(b.) 1 mol. of aniline was heated with varying quantities of acetic acid at  $155^{\circ}$ , and the following numbers indicating the percentage of the aniline converted into acetanilide were found:—

Proportion.	Coeff.	15 min.	1 hr.	24 hrs.	Limit (216 hrs.).
$1\text{C}_6\text{H}_7\text{N} + 1\text{C}_2\text{H}_4\text{O}_2$ ..	0.3921	34.71	58.28	79.17	79.68
$1\text{C}_6\text{H}_7\text{N} + 2\text{C}_2\text{H}_4\text{O}_2$ ..	0.5633	57.30	91.38	94.60	96.88
$1\text{C}_6\text{H}_7\text{N} + 4\text{C}_2\text{H}_4\text{O}_2$ ..	0.7207	78.08	96.64	98.12	99.80

The limit increases with increase in the quantity of acetic acid, and already with 4 mols. of the latter, the conversion is complete. The increase of the initial velocity is of a normal character, unlike that in case (a). B. B.

**Thiocarbamates.** By W. WILL (*Ber.*, 15, 1303—1309).—A continuation of the author's researches (this vol., p. 723). As the bases formed by the action of the alcoholic iodides on the thiocarbamides readily give off mercaptan, it is probable that the iodide at first attaches itself to the molecule with loosening of the double bond of the sulphur-atom, and then the resultant unstable combination gives

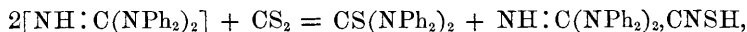
up a molecule of hydriodic acid. This view is supported by the isolation of the intermediate product formed by the direct addition of methyl iodide to the ethylene salt of phenyldithiocarbamic acid.

The *ethyl salt of phenyldithiocarbamate*,  $\text{CSSEt.NHPh}$ , is prepared by heating the base formed by the action of ethyl iodide on thiocarb-anilide, or by warming phenylthiocarbimide with ethyl mercaptan (Hofmann). It crystallises in colourless tables (m. p.  $60^\circ$ ), soluble in alcohol or benzene, insoluble in water and dilute acids, decomposed by concentrated alkalis with evolution of mercaptan, and by alcoholic ammonia or aniline with formation of phenylthiocarbamide or thiocarb-anilide.

The *amyl salt*, prepared by heating phenyl mercaptan with amylthiocarbimide, forms a leafy crystalline mass (m. p.  $71^\circ$ ), soluble in dilute alkalis, and undergoes the same reaction as the ethyl salt.

Rathke and Liebermann have shown that the aromatic thiocarb-amides and ethereal salts of phenylthiocarbamic acid are soluble in alkalis, and form silver salts which can be converted into a methyl salt of formula  $\text{SMe.C(OEt):NPh}$ . These reactions point to the presence of a sulphydryl group in thiocarbamide (cf. this vol., p. 724); but this view has been opposed by Bernthsen, who assigns to the silver salt the formula  $\text{CS(OEt).NAgPh}$ . In order to corroborate the former view, the author endeavoured to obtain a silver and methyl salt of ethyl phenyldithiocarbamate, but without success. V. H. V.

**Tetraphenylthiocarbamide.** By A. BERNTHSEN and G. FRIESE (*Ber.*, 15, 1530).—By the action of carbon bisulphide at  $260-270^\circ$  on tetraphenylguanidine, the authors have succeeded in obtaining this symmetrical compound according to the equation:



the latter compound being decomposed into diphenylamine and other products: the yield of the pure thiocarbamide is about 60 per cent. of the theoretical. By several times recrystallising the crude product from alcohol, it is obtained in long transparent yellowish needles (m. p.  $195^\circ$ ), which are insoluble in water, slightly soluble in cold, freely in hot alcohol. It is dissolved by sulphuric acid in the cold, and precipitated unchanged on dilution; when heated with the acid, it is decomposed, with evolution of sulphurous anhydride and formation of diphenylamine products. It is not decomposed by boiling with an alkaline solution of lead oxide, but on adding sodium amalgam the formation of lead sulphide is at once apparent. It is not altered by prolonged boiling with mercuric oxide, which is in harmony with the absence of amide hydrogen. Heated with aniline at the boiling point of the latter, no hydrogen sulphide is evolved, and therefore no pentaphenylguanidine is formed. When heated alone, it is decomposed at its boiling point with formation of diphenylamine, and probably phenyl sulphide.

That this body is tetraphenylthiocarbamide and not the isomeric phenylimidothiophenyldiphenylcarbamine,  $\text{NPh:C(SPh).NPh}_2$ , is proved by the absence of phenylmercaptan and aniline from the products of its decomposition by sulphuric acid (50 per cent.).

By the preparation of tetraphenylthiocarbamide and the previous preparation of ethylphenyldithiourethane,  $\text{NEtPh.CS.SEt}$ , the authors have established the typical connections of thiocarbamide and dithiocarbamic acid. The analogy of the monothio- with the dithio-carbamates strengthens the probability that the former also are derived from the normal type. The proof of the existence of two isomeric classes of the thiamides of carbonic acids, such as has been previously established by the authors for the thiamides of monobasic acids, is now complete for the first of the following groups, and is rendered probable for the second and third:—

- (1.) Thiocarbamides,  $\text{CS} \begin{smallmatrix} \text{NR}_2 \\ \text{NR}_2 \end{smallmatrix}$ , and imidothiocarbamates,  $\text{C}(\text{NH}) \begin{smallmatrix} \text{NR}_2 \\ \text{SR} \end{smallmatrix}$ .
- (2.) Dithiocarbamates,  $\text{CS} \begin{smallmatrix} \text{NR}_2 \\ \text{SR} \end{smallmatrix}$ , and imidodithiocarbonates,  $\text{C}(\text{NH}) \begin{smallmatrix} \text{SR} \\ \text{SR} \end{smallmatrix}$ .
- (3.) Thiocarbamates,  $\text{CS} \begin{smallmatrix} \text{NR}_2 \\ \text{OR} \end{smallmatrix}$ , and imidomonothiocarbonates,  $\text{C}(\text{NH}) \begin{smallmatrix} \text{SR} \\ \text{OR} \end{smallmatrix}$ .

The authors conclude with certain strictures of a personal character on recent publications of Will's on the carbon bisulphide reaction and cognate subjects.

C. F. C.

**Action of Alcoholic Iodides on Ditolyththiocarbamides.** By W. WILL and O. BIELSCHOWSKI (*Ber.*, **15**, 1309—1318).—The authors have examined the products formed by the action of alcoholic iodides on ortho- and para-tolyththiocarbamides, and obtained compounds homologous with those formed from phenylthiocarbamide (this vol., 723).

*Para-derivatives.*—*Paratolylimidotolylmethylthiocarbamate*,



is obtained by heating paradi-tolyththiocarbamide with methyl iodide in molecular proportions. It crystallises in colourless needles melting at  $128^\circ$ , easily soluble in sulphuric acid, insoluble in water. When heated, it decomposes with evolution of methyl mercaptan. It is converted by alkalis and hydrochloric acid into ditolylcarbamide, and on boiling with aniline, it yields phenylditolylguanidine.

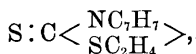
*Tolylthiomethylthiocarbamate*,  $\text{CSSMe.NH.C}_7\text{H}_7$ , is formed together with tolyththiocarbamide by heating the above base with carbon bisulphide; on removal of the thiocarbimide by distillation in a current of steam, the methylthiocarbamate is obtained in large prisms ( $84^\circ$ ) soluble in alcohol and ether, insoluble in water. When heated, it is decomposed into methyl-mercaptan and tolyththiocarbamide; with alcoholic ammonia, it forms monotolyl-, and with toluidine, ditolylthiocarbamide.

*Tolylmethylthiocarbamate*,  $\text{COSMe.NH.C}_7\text{H}_7$ , is obtained, together with toluidine, by heating the imidomethyl base with dilute sulphuric acid, thus:  $\text{NC}_7\text{H}_7 : \text{C}(\text{SMe}).\text{NH.C}_7\text{H}_7 + \text{H}_2\text{O} = \text{COSMe.NH.C}_7\text{H}_7 + \text{C}_7\text{H}_7.\text{NH}_2$ . It crystallises in colourless needles melting at  $107^\circ$ , easily soluble in alcohol or ether, insoluble in water. When boiled with ammonia, it gives monotolyl-, and with toluidine, ditolylthiocarbamide with evolution of methyl mercaptan.

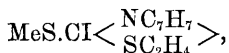
*p*-Tolylimidotolylethylthiocarbamate,  $\text{NC}_7\text{H}_7:\text{C}(\text{SEt})\text{NH}\cdot\text{C}_7\text{H}_7$ , is formed in a manner similar to the corresponding methyl compound; it crystallises in colourless needles melting at  $87^\circ$ ; forms crystalline compounds with hydrochloric and sulphuric acids; and in its reactions is analogous to the methyl compound.

Tolylthioethylthiocarbamate,  $\text{CSSEt}\cdot\text{NH}\cdot\text{C}_7\text{H}_7$ , crystallises in needles (m. p.  $74^\circ$ ); tolylethylthiocarbamate crystallises in needles (m. p.  $79^\circ$ ), insoluble in alkalis; it differs from the isomeride described by Lieberman in not forming methyl ethyl ether on warming with methyl iodide and alkali.

Tolylimidotolylethylenethiocarbamate,  $\text{NC}_7\text{H}_7:\text{C}<\begin{smallmatrix}\text{NC}_7\text{H}_7 \\ \text{SC}_2\text{H}_4\end{smallmatrix}>$ , is formed by dissolving ditolylthiocarbamate in ethylene bromide; it crystallises in leaflets melting at  $112^\circ$ , soluble in hot alcohol; gives crystalline salts with acids. The corresponding dithiocarbamate,



forms light golden crystals melting at  $126^\circ$ , insoluble in dilute acids and alkalis. It combines directly with methyl iodide to form a compound,



crystallising in prisms, which is decomposed by alkalis or silver oxide, yielding ethylene thiocarbamate; and, on boiling with ammonia or the amines, gives derivatives of imidotolylethylenecarbamate.

Tolylethylenethiocarbamate,  $\text{O}:\text{C}<\begin{smallmatrix}\text{NC}_7\text{H}_7 \\ \text{SC}_2\text{H}_4\end{smallmatrix}>$ , crystallises in long delicate needles melting at  $88^\circ$ , insoluble in dilute acids and alkalis.

The *ortho*-derivatives were prepared by the same processes as those for the *para*-derivatives; they are described shortly below.

Tolylimidotolylmethylthiocarbamate, colourless needles (m. p.  $60^\circ$ ); the *ethyl* salt, needles (m. p.  $151^\circ$ ); tolylmethylthiocarbamate, leaflets (m. p.  $70^\circ$ ); the *ethyl* salt, glistening tables (m. p.  $66^\circ$ ); tolylthioethylthiocarbamate, thick prisms (m. p.  $72^\circ$ ). Tolylimidotolylethylenethiocarbamate, glistening leaflets (m. p.  $91^\circ$ ); tolylthioethylthiocarbamate melts at  $129^\circ$ . It combines directly with methyl iodide to form a compound crystallising in prisms (m. p.  $151^\circ$ ), analogous to the *para*-derivative.

V. H. V.

**Thiocarbamides of Phenylhydrazine.** By E. FISCHER and E. BESTHORN (*Annalen*, **212**, 316—333). — Diphenylthiocarbazide,  $\text{C}_{13}\text{H}_{14}\text{N}_4\text{S}$ , a compound described in a former paper (*Annalen*, **190**, 118; *C. J.*, 1878, Abstr., 308), is remarkable for the facility with which it is converted, under various circumstances, into a colouring matter, consisting of diphenylthiocarbazone,  $\text{C}_{13}\text{H}_{12}\text{N}_4\text{S}$ , the change consisting, as will be presently explained, in the conversion of a hydrazine-group  $\text{—NH—NH—}$  into an azo-group  $\text{—N=N—}$ . When finely pulverised diphenylthiocarbazide is boiled for 10—15 minutes with moderately strong alcoholic potash, it dissolves, with exception of a small quantity of dark-coloured resin; and the dark-red



filtered liquid, on addition of dilute sulphuric acid, deposits the diphenylthiocarbazone in blue-black flocks, together with another product to be described further on. To remove the latter, the mass freed from mother-liquor is lixiviated with dilute soda-ley; the filtrate is again precipitated by sulphuric acid; and, for further purification, the product, after washing with water and pressing between filter-paper, is dissolved in warm chloroform, and precipitated from the concentrated solution by alcohol. The physical properties of this thiocarbazone have been already described (*loc. cit.*). It has decidedly the characters of an acid; its compounds with the alkalis and alkaline earths are easily soluble in water, and have a dark-red colour. Its alkaline solution is easily decolorised by zinc-dust, even at ordinary temperatures; but on removal of the zinc, it quickly turns red-violet in contact with the air, and, after acidulation, deposits red crystalline flocks, consisting of an insoluble lac-like compound of the thiocarbazone with zinc oxide,  $(C_{13}H_{12}N_4S)_2ZnO$ , which may also be regarded as a monohydrate of the normal zinc salt,  $(C_{13}H_{11}N_4S)_2Zn \cdot H_2O$ . This zinc-salt dissolves with moderate facility in hot chloroform, less readily and with purple-red colour in benzene, more readily in dilute acids, forming a zinc-alkalimetal salt, from the solution of which the free thiocarbazone is precipitated by hot strong hydrochloric acid. The same decomposition is effected by heating the dry zinc-salt with strong acids. The silver, mercury, and lead compounds of diphenylthiocarbazone are likewise insoluble in water.

The formation of diphenylthiocarbazone by the action of alkalis on the corresponding thiocarbazide consists in a simultaneous oxidation and reduction, analogous to that which takes place in the resolution of an aldehyde under the influence of alkalis into an acid and an alcohol, one part of the thiocarbazide being converted by loss of hydrogen into the thiocarbazone, while another portion is resolved, with assumption of hydrogen, into aniline and a compound  $C_7H_9N_3S$ , to be described further on:  $2C_{13}H_{11}N_4S = C_{13}H_{12}N_4S + C_6H_7N + C_7H_9N_3S$ .

In accordance with the constitution of the carbamides of phenylhydrazine (*Abstr.*, 1878, 307), that of diphenylthiocarbazide may be represented by the formula  $PhNH.NH.CS.NH.NHPh$ , and its conversion into the thiocarbazone results from the oxidation of one of the hydrazine-groups  $-NH.NH-$ : consequently, the thiocarbazone must be represented by the formula  $PhN:M.CS.NH.NHPh$ , which likewise affords a satisfactory representation of all known transformations of this compound.

*Oxidation of Diphenylthiocarbazone.*—When a solution of this compound in alcoholic potash is heated on the water-bath, and hydrated manganese dioxide is added, with frequent agitation, the colour of the liquid changes from dark to light red; and if the solution be then filtered and left to cool, it deposits a portion of the oxidation-product in small red needles, while the rest remains mixed with the manganese oxide, and may be extracted therefrom by boiling with alcohol. This product, purified by recrystallisation from hot alcohol, has the composition of *diphenylthiocarbodiazone*,  $C_{13}H_{10}N_4S = PhN:N.CS.N:NPh$ , and is formed by oxidation of the second hydrazine-group of the thiocarbazide to an azo-group. It differs from diphenylthiocarbazone in

the absence of acid properties. It is insoluble in alcohol, sparingly soluble in ether and in benzene, easily soluble in chloroform and in hot alcohol. When heated, it detonates before fusing. By careful reduction in alcoholic solution with a small quantity of zinc-dust, it is converted into diphenylthiocarbazono, as shown by the splendid purple colour of the resulting zinc-salt; but on prolonged action this colour disappears in consequence of further reduction.

*Reduction of Diphenylthiocarbazono.*—When the dark-red solution of this colouring matter in cold dilute soda-ley is treated with zinc-dust, it first acquires a splendid red-violet colour, due to the formation of the zinc sodium salt already mentioned. If, however, the quantity of zinc-dust present be not too small, this colour disappears completely on agitation, but reappears where the solution comes in contact with the air. On filtering the colourless solution into dilute acetic acid, a light red crystalline precipitate is formed, consisting of diphenylthiocarbazono,  $C_{13}H_{14}N_2S$ . If, on the other hand, the decolorised alkaline liquid be heated on the water-bath together with the zinc-dust, it does not afterwards become coloured in contact with the air, and the alkaline solution contains, no longer a trace of diphenylthiocarbazono, but only aniline and the body  $C_7H_9N_3S$ , which, as already observed, is formed as a bye-product in the preparation of diphenylthiocarbazono. If the reduction with soda and zinc-dust takes place in alcoholic solution, the compound remains dissolved in the warm liquid, and separates on cooling, after removal of the zinc-dust, in faintly coloured needles, and may be obtained by recrystallisation from hot alcohol in small white prisms melting at  $200-201^\circ$ . This compound is *phenylthiosemicarbazide*,  $NH_2.CS.NH.NHPh$ . Its formation, together with aniline and diphenylthiocarbazono by heating the thiocarbazono with alcoholic or aqueous potash, has been already noticed (p. 1092). It is also produced by heating the thiocarbazono with alkali and zinc-dust, and directly from phenylhydrazine by the action of thiocyanic acid; on agitating this base with aqueous thiocyanic acid, the slightly soluble thiocyanate separates in colourless laminæ; but on heating the dry salt in the oil-bath to  $160-170^\circ$ , a brisk evolution of ammonia takes place, and the melt solidifies to a crystalline mass, which, when lixiviated with cold water, leaves nearly pure phenylthiosemicarbazide. The reaction, however, takes place much more definitely on heating phenylhydrazine hydrochloride and ammonium thiocyanate together in alcoholic solution, whereby a crystalline mixture of sal-ammoniac and phenylthiosemicarbazide is obtained; and on filtering, washing out the sal-ammoniac with cold water, and crystallising the residue once or twice from boiling alcohol, the phenylthiosemicarbazide is obtained pure.

Phenylthiosemicarbazide dissolves sparingly in ether, benzene, and chloroform, much more readily in hot alcohol, from which it separates on cooling in well-defined monoclinic prisms, having the axial ratio  $a : b : c = 2.6028 : 1 : 1.4714$ , and the angle  $ac = 83^\circ 49'$ . Observed faces  $0P$ ,  $P$ ,  $\infty P\infty$ ,  $2P\infty$ ,  $2P$ . The crystals are prismatically elongated in the direction of the orthodiagonal, and always developed at one end only. The compound melts with incipient decomposition at  $200-201^\circ$ . It is indifferent to acids, and is not altered by boiling with

dilute hydrochloric or sulphuric acid. It is readily dissolved on heating with strong potash-ley, the solution on cooling depositing a well-crystallised salt, which is decomposed by water with formation of thiocarbamide. With mercuric chloride and ammoniacal silver-solution, the aqueous solution gives white precipitates, which blacken after some time. Ferric chloride oxidises the compound, with separation of sulphur.

*Phenylthiocarbazine*,  $C_7H_6N_2S = CS \begin{matrix} \text{NH} \\ \diagup \\ | \\ \text{N} \cdot C_6H_5 \end{matrix}$ , is obtained by heating

phenylthiosemicarbazide (10 g.) with (30 c.c.) hydrochloric acid of 20 per cent. in sealed tubes at  $125-130^\circ$  for 12 hours. On leaving the contents of the tubes to cool, the hydrochloride of the thiocarbazine separates for the most part in tufts of pale-yellow needles, which must be strained on a pump-filter, dissolved in a small quantity of warm water, decolorised with animal charcoal, and precipitated from the filtrate by a stream of gaseous hydrochloric acid. On mixing the pure white salt with an alkali, the sparingly soluble base separates in colourless flocks, and may be obtained by recrystallisation from water in thin silvery laminae. It melts at  $129^\circ$ , distils in small quantities without decomposition, dissolves readily in alcohol, ether, and chloroform, very sparingly in cold water. It unites with acids, forming well-crystallised salts. The *hydrochloride*,  $C_7H_6N_2S \cdot HCl$ , is readily soluble in water, and separates on addition of strong hydrochloric acid in white slender needles, dissolves readily in alcohol, and is precipitated therefrom by ether. It melts at  $240^\circ$ . The *platinochloride*,  $(C_7H_6N_2S)_2H_2PtCl_6$ , crystallises from hot water in oblique yellow prisms. The easily soluble *sulphate* crystallises in tufts of needles. The *chromate*, which is nearly insoluble, separates in thin red needles on adding chromic acid to an acid solution of the base, and is not attacked by boiling water. The *picrate* is sparingly soluble in water, and crystallises in slender yellow needles. Phenylthiocarbazine is indifferent to alkalis; but on adding its aqueous solution to an ammoniacal solution of silver, a white flocculent precipitate is formed, having the composition  $C_7H_5N_2SAg$ .

Phenylthiocarbazine is distinguished from most other hydrazine-compounds by its greater stability. Most of the ordinary reducing agents have no effect upon it; but when heated at  $200^\circ$  with fuming hydriodic acid and phosphonium iodide, it is decomposed, with formation of carbonic anhydride, hydrogen sulphide, ammonia, and aniline. It is almost equally indifferent to oxidising agents, and may be boiled for a long time without alteration with Fehling's solution, mercuric oxide, ammoniacal silver solution, or chromic acid and dilute sulphuric acid. Permanganic acid, on the other hand, oxidises it rapidly, both in acid and in alkaline solution, converting all the sulphur into sulphuric acid. An equally energetic action is exerted by bleaching powder or alkaline hypochlorites, the solutions of which immediately produce, with a cold aqueous solution of the base, a dark violet flocculent precipitate, insoluble in most solvents, but dissolving with deep red colour in strong sulphuric acid. This reaction is very characteristic, and may serve for the detection of the base.

*Monacetyl-phenylthiocarbazine*,  $\text{CS} \begin{array}{c} \text{N}^{\text{Ac}} \\ | \\ \text{N}^{\text{Ph}} \end{array}$ , is formed by heating the

base for a short time with acetic anhydride, and partly separates in crystals on cooling. The rest may be obtained by repeatedly heating the liquid with alcohol on the water-bath to expel the excess of acetic acid, and crystallising the residue from boiling alcohol. In this manner, colourless tabular crystals are obtained, very soluble in hot alcohol, sparingly in water, melting at  $187^{\circ}$ .

The corresponding *benzoyl-compound*, obtained by heating the base with benzoic chloride, forms colourless crystals melting at  $186^{\circ}$ .

*Methylphenylthiocarbazine*,  $\text{CS} \begin{array}{c} \text{N}^{\text{Me}} \\ | \\ \text{N}^{\text{Ph}} \end{array}$ .—The hydriodide of this base

is formed when phenylthiocarbazine is heated with twice its weight of methyl iodide in a sealed tube at  $100^{\circ}$  for 10 or 12 hours. On decomposing this salt with an alkali, the methyl-base separates in white flocks, and may be obtained by recrystallisation from hot water in colourless plates, melting at  $123^{\circ}$ , very slightly soluble in water, readily in alcohol, ether, and chloroform. It volatilises without decomposition, and is distinguished from the non-methylated base by not being attacked by nitrous acid, even at the boiling heat.

*Bromophenylthiocarbazine*,  $\text{C}_7\text{H}_5\text{N}_2\text{SBr}$ , is formed on mixing the cold very dilute chloroform-solutions of phenylthiocarbazine and bromine, and separates immediately in crystals; and on washing these with chloroform, dissolving them in sulphurous acid, and supersaturating with an alkali, the bromine-compound separates in very slender white needles, which, after recrystallisation from dilute alcohol, melt at  $210^{\circ}$ .

H. W.

**Oxidation of Metatoluenesulphonamide.** By I. REMSEN and C. PALMER (*Amer. Chem. J.*, **4**, 122—124).—Metatoluenesulphonamide was prepared by introducing a sulpho-group into orthobromotoluene, and then replacing the bromine by hydrogen, by the action of sodium-amalgam on the aqueous solution of the sodium salt. On neutralising the resulting liquid with sulphuric acid and concentrating, a large quantity of sodium sulphate separated out, and after as much as possible of this had been removed, the last mother-liquor was evaporated to dryness, the dried residue treated with phosphorus pentachloride, and the resulting sulphochloride converted by boiling with aqueous ammonia into the sulphonamide,  $\text{C}_6\text{H}_4(\text{CH}_3)(\text{SO}_2\text{NH}_2)$ . The product was, however, mixed with orthotoluenesulphonamide, the presence of which was due to that of parabromotoluene in the orthobromotoluene employed; for when sulphuric acid acts on *p*-bromotoluene, the product contains the sulpho-group in the ortho-position relatively to the methyl, so that when the bromine is removed, the product must be *o*-toluenesulphonamide. The meta-amide, after purification, exhibited the properties ascribed to it by Hübner and Muller (*Annalen*, **169**, 47), and melted at  $90$ — $91^{\circ}$ .

By oxidation with potassium permanganate in alkaline solution, and by chromic acid mixture, metatoluenesulphonamide is converted

into metasulphamine-benzoic acid,  $\text{C}_6\text{H}_4(\text{COOH})^1(\text{SO}_2\text{NH}_2)^3$ , identical with the so-called "sulphobenzamic acid," which is obtained by treating sulphobenzamide or ammonium ethyl sulphobenzoate with potassium hydroxide (Limpricht and v. Uslar, *Annalen*, **106**, 27), and by the action of sulphuric oxide on benzonitril (Engelhardt, *J. pr. Chem.*, **75**, 363).

The oxidation of metatoluenesulphonamide by potassium permanganate does not take place readily. The same is the case with the para-amide, whereas the ortho-amide is very easily oxidised by the same reagent.

H. W.

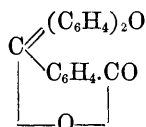
**Phenolphthaleïn Anhydride and the Constitution of Fluoresceïn.** By A. BAEYER (*Annalen*, **212**, 347—353).—The difference in chemical character of the phenols arising from differences in the relative position of the hydroxyl-groups, is especially conspicuous in their compounds with phthalic anhydride. Among these differences, the most important is that all the phthaleïns derived from di- or trihydroxylated benzenes give up water, the elements of which are furnished by two phenolic hydroxyls, which is not the case with ordinary phenolphthaleïn. Now since the latter—as shown by the formation of *p*-dihydroxybenzophenone by fusing it with potash—is a *para*-derivative, it may be inferred that the hydroxyl-group in the para-position is not disposed for the formation of an anhydride, and further that hydroxyls situated in the ortho- or meta-position are favourably disposed to that transformation. Whether the ortho- and meta-positions of the hydroxyls exhibit any difference in the facility with which they allow of the elimination of water cannot at present be determined, as both appear to admit of the formation of anhydrides. Hydroquinone-phthaleïn cannot be employed for the determination of this question, since its hydroxyls are in the ortho-meta-position; but phenolphthaleïn anhydride, obtained as a secondary product in the preparation of phenolphthaleïn, appears to be better adapted for the purpose.

In the preparation of phenolphthaleïn by heating phthalic anhydride with sulphuric acid, there is obtained, as secondary product, a dirty-looking mass insoluble in alkalis, from which by alternate boiling with alkalis and recrystallisation from alcohol with addition of animal charcoal, there is obtained a colourless substance which crystallises in large flat deeply striated needles melting at 173—175°. This substance is the anhydride of phenolphthaleïn,  $\text{C}_{20}\text{H}_{12}\text{O}_3$ . It is not attacked by alcoholic potash; dissolves without alteration, and with strong greenish-yellow fluorescence, in strong sulphuric and nitric acids; and is nitrated by heating with a mixture of the acids. With bromine dissolved in glacial acetic acid, it yields a dibromophthaleïn anhydride,  $\text{C}_{20}\text{H}_{10}\text{Br}_2\text{O}_3$ , melting at 255—258°, very slightly soluble in alcohol.

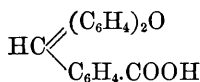
*Phenolphthalin anhydride*,  $\text{C}_{20}\text{H}_{14}\text{O}_3$ , obtained by treating the phthaleïn anhydride with alcoholic soda-ley, alcohol, and zinc-dust, crystallises from alcohol in small needles, dissolves readily in dilute alkalis and their carbonates, also in ether, more sparingly in benzene. Strong

sulphuric acid dissolves it on moderate heating, with yellow colour, quickly changing to green, and on further heating to cherry-red; and on pouring this red solution into water, a red-brown precipitate is obtained which resembles ferric hydrate in appearance, and dissolves in ether with bright fluorescence resembling that of an ammoniacal solution of fluoresceïn. Phenolphthalin anhydride dissolves in hot concentrated alkalis, the solutions on cooling depositing the corresponding alkali-salts. It is not acted on by phosphorus pentachloride at 100°. It melts at 214–217°.

The anhydrides of phenolphthaleïn and phenolphthalin are represented by the following constitutional formulæ:—

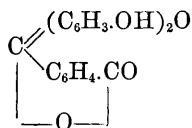


Phenolphthaleïn anhydride.

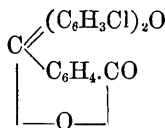


Phenolphthalin anhydride.

*Constitution of Fluoresceïn.*—According to the author's latest investigations (*Annalen*, 202, 36), this substance is the dihydroxy-phenolphthaleïn anhydride represented by the first of the following formulæ, and the corresponding chloride, or dichlorophthaleïn anhydride, is represented by the second formula:—

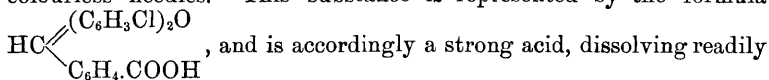


Fluoresceïn.



Chloride.

*Phthalin of Fluoresceïn Chloride.*—This chloride offers considerable resistance to the action of alkalis, separating unaltered for example, on evaporation from its solution in soda-ley. Nevertheless this solution contains a salt of a substituted triphenyl-carboxylic acid, inasmuch as zinc-dust under the same conditions as with phenolphthaleïn anhydride, separates from it a derivative of triphenylmethane-carboxylic acid, viz., the *phthalin of fluoresceïn chloride*. To prepare this substance, a solution of fluoresceïn chloride in an alcoholic soda-solution containing a large quantity of alcohol is mixed with water to incipient turbidity, and boiled with zinc-dust, with gradual addition of water, till all the alcohol is driven off. The zinc-dust is then filtered off and washed with water, and the filtrate is treated with dilute sulphuric acid, which throws down the phthalin in white curdy flocks, which by solution in alcohol and precipitation with water may be converted into colourless needles. This substance is represented by the formula



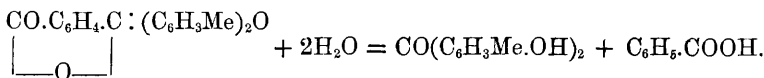
in dilute alkalis and their carbonates. It melts at 226° and dissolves in alcohol, ether, benzene, and acetone, but not in light petroleum. Strong



some time, in combination with the alkali, sometimes in laminar crystals, sometimes in flocks. It melts at  $210^{\circ}$ , and when slowly heated sublimes without decomposition. It is a very stable compound, not being altered by remaining for months in contact with the air. It dissolves with rise of temperature in strong sulphuric acid, forming a brown solution from which water throws down chocolate-brown flocks, which dissolve in ether with yellow colour and splendid reddish-green fluorescence. The body thus formed, which is perhaps a phthalidein, decomposes quickly; and appears not to be rendered more stable by bromination or acetylation; neither could a phthalidein be obtained from it by oxidation.

*Products of the Decomposition of Paracresolphthalein Anhydride by Fusion with Potash.*—When the anhydride is fused with potash at a moderate heat, part of it dissolves on treating the melt with water, and acids added to the solution throw down *p*-cresol-phthalein: hence it appears that the anhydride takes up 1 mol. water when fused with potash: if however the temperature be raised above  $200^{\circ}$ , the product cakes together after some time into resinous lumps, and if the operation be then interrupted, the greater part of the product dissolves to a yellow liquid, which becomes milky on addition of an acid. On mixing this milky liquid with alcohol and boiling till the solution has become clear again, it deposits after some time splendid yellow needles which, remembering the behaviour of phenolphthalein when fused with potash, may safely be regarded as a *dimethyl-dihydroxybenzophenone* having the constitution  $\text{CO}(\text{C}_6\text{H}_3\text{Me.OH})_2$ .

On distilling the acidulated solution of the melt in a current of steam, benzoic acid passes over. Consequently the decomposition of paracresolphthalein anhydride by fusion with potash may be represented by the equation—



Dimethyl-dihydroxybenzophenone melts at  $104\text{--}105^{\circ}$ , and volatilises undecomposed at a higher temperature. It is insoluble in water and in dilute acids, but dissolves readily in caustic alkalis, alcohol, and ether.

*Condensation-products of Paracresolphthalein Anhydride by concentrated Sulphuric Acid.*—When this phthalein anhydride, or a mixture of paracresol and phthalic anhydride, is heated for some time at  $200^{\circ}$  with a large quantity of strong sulphuric acid, there is formed, exactly as in the case of the corresponding phenol-compound, an anthraquinone-derivative, which may also be prepared by heating 1 part *p*-cresol, 1 part phthalic anhydride, and 20 parts strong sulphuric acid for about two days, the temperature being slowly raised from  $160^{\circ}$  to  $200^{\circ}$ . The flocks thrown down by water are separated by filtration, then dried and exhausted with ether; the residue is dissolved in potash; barium chloride is added; and the resulting barium-lake is decomposed by hydrochloric acid. The body thus obtained was too small in quantity for analysis, but its reactions show it to be a methyl-erythroxyanthraquinone, inasmuch as it forms with baryta-water a



dark red-violet lake, which is decomposed by carbonic acid; dissolves in alkalis with violet-red colour, like that obtained with erythro-hydroxyanthraquinone; is insoluble in cold strong aqueous ammonia, somewhat soluble in the same when warm; sublimes in reddish-yellow needles; and when quickly heated yields oily drops which quickly solidify in radio-crystalline forms. Consequently the body in question is a *methylerythro-hydroxyanthraquinone* represented by the formula  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} C_6H_2(CH_3)(OH)$ . This affords a new demonstration of the correctness of Baeyer's formulæ of the hydroxyanthraquinones, according to which paracresol must necessarily yield a methylerythro-hydroxyanthraquinone; whereas orthocresol should yield an ordinary methyl-hydroxyanthraquinone, and according to Fraude's investigations (*Annalen*, **202**, 153, Abstr., 1879, 635), actually does so.

H. W.

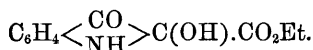
**Artificial Indigo.** (*Chem. Centr.*, 1882, 366.)—The group of alkaline reducing agents, which like grape or milk sugar, effect the conversion of orthonitrophenylpropionic acid into artificial indigo, includes, according to further investigations of the Baden Aniline and Soda-works, the sulphides, sulphydrates, polysulphides, thio-carbonates, and ethereal thio-carbonates of the alkalis and alkaline earths, and especially the alkaline xanthates. These reducing agents act already in the cold and more quickly on warming the aqueous or alcoholic solution. When xanthates are used, the formation of artificial indigo takes place to a great extent after the solution has been evaporated. Thus, *e.g.*, the addition of an alkaline sulphydrate to a solution of an alkaline salt of orthonitrophenylpropionic acid, causes the separation of a precipitate, which besides indigo and free sulphur contains violet and red dye-stuffs soluble in alcohol, belonging to the indigo-group. The reaction is still more energetic when a concentrated solution of an alkaline polysulphide is added to a concentrated solution of an alkaline orthonitrophenylpropionate. When xanthates are used, the following process is adopted:—1 kilo. orthonitrophenylpropionic acid is suspended in about half the quantity of water, treated with 0.5 kilo. potassium carbonate, and after neutralising, 1.5 kilo. potassium xanthate is added, and the mixture agitated thoroughly. It is then dried at the ordinary temperature. The colouring matter forms rapidly, and when the presence of unaltered orthonitrophenylpropionic acid can no longer be detected, the reaction is complete. The dark blue product is then washed with water, collected and dried. It is purified with suitable solvents such as carbon bisulphide or alcohol. The same reducing agents, especially the xanthates, can be used for producing artificial indigo direct on the fibre. The formation of colouring matter takes place also in the cold after drying, and more quickly in a drying chamber.

D. B.

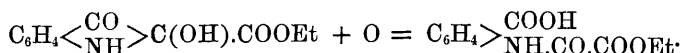
**Compounds of the Indigo-group.** By A. BAEYER (*Ber.*, **15**, 775—787).—Part III.—Ethyl indoxylate is converted by oxidation into three compounds, which may be regarded as presenting different stages of oxidation. (1.) *Ethyl indoxanthidate*,  $C_{22}H_{20}N_2O_6$ ; (2) *ethyl indoxanthinate*,  $O_{11}H_{11}NO_4$ ; (3) *ethyl oxalylanthranilic acid*,  $C_{11}H_{11}NO_5$ .

The second of these compounds is obtained by the careful oxidation of ethyl indoxylate dissolved in acetone, with ferric chloride at 60°. The product yields this compound to ether, forming a solution having a slight green fluorescence, from which it may be obtained by recrystallisation in light yellow needles, m. p. 107°. When boiled with alkalis, it is resolved into orthamidobenzoic acid. Its aqueous solutions when treated with acids give an amorphous yellow precipitate, having the composition  $C_{22}H_{20}N_2O_7$ , which is soluble in alkalis, forming a green solution in which acids produce an indigo-coloured precipitate.

*Ethyl nitroso-indoxanthinate*,  $C_{11}H_{10}(NO)NO_4$ , is obtained by acting on ethyl indoxanthinate with sodium nitrite and sulphuric acid. It is sparingly soluble in water, but easily soluble in alcohol, ether, and glacial acetic acid, and melts with evolution of gas at 113°. By reducing agents it is converted into ethyl indoxylate; it yields Liebermann's reaction, and is, therefore, a nitrosamine, and consequently ethyl indoxanthinate must contain an imido-group, and its constitution may be represented as follows:—

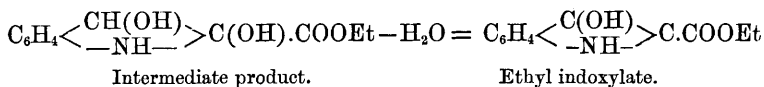


*Ethyl-oxalylanthranilic acid* is the final product of the action of potassium dichromate and sulphuric acid on ethyl indoxylate; it crystallises from alcohol in colourless needles, melting at 180–181°. Hydrochloric acid resolves it into oxalic and orthamidobenzoic acids. Its production may be represented by supposing it to be the product of oxidation of ethyl indoxanthinate, thus:—



The formation of this body is analogous to the production of acetyl amidobenzoic acid from methylketol (*Ber.*, 14, 879): further by oxidation with ferric chloride, methylketol appears to yield a compound analogous to ethyl indoxanthinate.

II. *Reduction of Ethyl Indoxanthinate*.—By reduction with zinc-dust and acetic acid, or by hydriodic acid, this compound is converted into ethyl indoxylate, which may be represented as taking place in two stages: (1) the addition of hydrogen, (2) a loss of 1 mol. of water—a representation analogous to that used to explain the formation of methyl-ketol from amidobenzylmethylketone, thus:—



From this it would appear that the constitution formerly assigned to ethyl indoxylate is not correct.

III. *Constitution of Ethyl Isatogenate*.—Reducing agents convert this compound into ethyl indoxylate, a fact yielding but little insight into the constitution of this compound. Ethyl isatogenate is, however, formed by treating ethyl indoxanthinate with ferrous chloride or

sulphate, and consequently ethyl isatogenate is supposed to have the following constitution :  $C_6H_4 \begin{array}{c} \text{CO.C.CO.OEt} \\ \diagup \quad \diagdown \\ \text{N} \quad \text{O} \end{array}$  It will be seen that

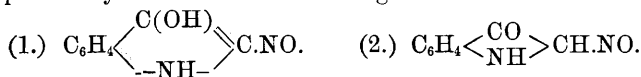
it contains the group  $\begin{array}{c} \text{N}-\text{C} \\ \diagup \quad \diagdown \\ \text{O} \end{array}$ , which the author styles "carbazoxy-group," in which, by the addition of a molecule of hydrogen, an amido-group and a hydroxyl-group are formed. This formula explains the formation of azoxybenzoic acid when ethyl isatogenate is treated with alkalis.

#### IV. Action of nitrous acid on the members of the indoxyl-group.

*Nitrosamine of Ethyl-indoxyl*,  $C_6H_4 \begin{array}{c} \text{C(OEt)} \\ \diagup \quad \diagdown \\ \text{N(NO)} \end{array} \text{CH}$ , is obtained by

acting on an alcoholic solution of indoxyl with acetic acid and sodium nitrite; it forms pale yellow slender needles, melting at 84—85°, is insoluble in water and alkalis, but soluble in alcohol, &c., and is converted by reducing agents into ethylindoxyl. Ethyl indoxylate, treated with nitrous acid, forms three products, all of which are insoluble in alkalis. The chief product has the formula  $C_{22}H_{18}N_4O_8$ , and is probably a dinitrosamine of ethyl indoxylate; it melts at 173°. Of the other two products, one melts at 120° and the other at 143°.

*Nitrosindoxyl* is obtained by the action of nitrous acid on ethyl indoxyllic acid. In a former communication (*Ber.*, **14**, 1743) the formula  $C_{11}H_{10}(NO)NO_4$  was assigned to this compound; further examination of the same has, however, shown that its composition is expressed by the formula  $C_8H_6(NO).NO$ . In the production of this compound it would appear that ethylindoxyllic acid loses carbonic anhydride, and that the ethyl-group is replaced by hydrogen. Its constitution may be expressed by one of the two following formulæ:—



According to the first, it is a nitroso-derivative of oxindol; according to the second, a nitroso-derivative of a reversed oxindole. The former of these is regarded as the more correct, inasmuch as this compound possesses the characters of a feebly dibasic acid, also the characters of a phenol, and forms an ethyl salt having acid properties. It is not a nitrosamine, since it does not yield Liebermann's reaction. By reducing agents, nitroso-indoxyl does not form indoxyl, but a product which is probably an amido-indoxyl, since, when treated with ferric chloride, it forms isatin. The fact that indole is converted in the animal organism into indoxyl, together with the phenol-like characters of this latter, would make it appear that indoxyl is a hydroxylated indole. Now the action of nitrous acid on indoxyl reveals the presence in it of an amido-group, so that indole must also contain this group. The presence of this group has been shown by treating an alcoholic solution of dichlorindole (*Ber.*, **12**, 456) with caustic soda and methyl iodide, whereby a compound,  $C_8H_7Cl_2N$ , was obtained; it is insoluble in alkalis, and, like dichlorindole, reddens pine-wood moistened

with hydrochloric acid. It is insoluble in nitrous acid, and crystallises from alcohol in lustrous needles, melting at 58—59°. Its properties prove it to have the constitution  $C_6H_4 \begin{array}{c} \diagup CCl \\ \diagdown NMe \end{array} CCl$ , and hence di-

chlorindole must be  $C_6H_4 \begin{array}{c} \diagup CCl \\ \diagdown NH \end{array} CCl$ , and indole must have the for-

mula  $C_6H_4 \begin{array}{c} \diagup CH \\ \diagdown NH \end{array} CH$  assigned to it several years ago by the author.

P. P. B.

**Action of Copper on Benzotrichloride.** By U. HANHART (*Ber.*, 15, 898—901).—When pure copper (free from oxide), in the form of powder, is moistened with benzotrichloride and warmed on a water-bath, an energetic reaction takes place, and two isomeric dichlorotolanes,  $C_{14}H_{10}Cl_2$ , are produced. The crystals melt at 60° and 140° respectively. On distillation with a large excess of copper, the dichlorotolanes are converted into tolane, and by the action of hydriodic acid and amorphous phosphorus at 170°, they are converted into dibenzyl,  $C_{14}H_{14}$ .

When a mixture of benzotrichloride (1 part) and benzene (2 parts) is boiled with 3 parts of copper-dust, tolane tetrachloride is produced.

W. C. W.

**Some Derivatives of Carbazole (Imidodiphenyl).** By G. L. CIAMICIAN and P. SILBER (*Gazzetta*, 1882, 272—280).—*Carbazole-carboxylic* or *Carbazolic acid*,  $C_{13}H_9NO_2 = C_{12}H_8N.CO_2H$ , is prepared by heating potassium-carbazole,  $C_{12}H_8KN$  (obtained by fusing carbazole with potassium hydroxide) at 270°, and passing a current of dry carbonic anhydride through the fused mass, which gradually solidifies. The product is treated with water, which dissolves the potassium carbazolate, leaving the unaltered carbazole; and on filtering and treating the concentrated filtrate with dilute sulphuric acid, the carbazolic acid is obtained in the form of a copious, whitish, flocculent precipitate. For purification, it is redissolved in potassium carbonate; the solution is boiled with animal charcoal and reprecipitated by sulphuric acid; the precipitate, after washing with water and drying in the exsiccator, is macerated, with occasional heating, in a quantity of alcohol not sufficient to dissolve it completely; and the solution is filtered after cooling, this series of operations being repeated fifteen or twenty times. Lastly, the residue left on evaporating the alcohol is sublimed at 150—160°; the sublimate, still containing traces of carbazole, is dissolved in potassium carbonate; and the acidified filtrate is treated with ether, which dissolves the carbazolic acid, and leaves it on evaporation in the form of a nearly white powder. On dissolving this in boiling alcohol and leaving the solution to cool slowly, the acid is finally obtained in colourless scales or flattened prisms having a nacreous lustre and faint blue fluorescence.

Carbazolic acid melts at 271—272°; it is nearly insoluble in water

whether cold or boiling, slightly soluble in cold, more soluble in boiling alcohol, easily in ether. It does not react like carbazole with nitric acid. It is sublimable, but when suddenly heated splits up into carbazole and carbonic anhydride, still more readily when heated with lime. Its silver salt,  $C_{13}H_8AgNO_2$ , is a white precipitate. The barium salt,  $(C_{13}H_8NO_2)_2Ba$ , likewise obtained by precipitation, forms white scales nearly insoluble in water, and having a nacreous lustre.

*Bromacetyl-carbazole*,  $C_{12}H_7BrN\overset{O}{\overset{||}{C}}Ac$ , is obtained by heating Graebe's acetyl-carbazole (*Annalen*, **163**, 343) dissolved in carbon bisulphide with a molecular proportion of bromine at  $100^\circ$  in a reflux apparatus, and remains, on distilling off the solvent, as a yellow crystalline mass, which by repeated crystallisation from the same solvent, yields the compound in colourless lamellæ, melting at  $128^\circ$ , very soluble in boiling alcohol and toluene, and separating therefrom completely on cooling; sparingly soluble in ether. It is not decomposed by aqueous potash, but when boiled with excess of alcoholic potash it yields:

*Bromocarbazole*,  $C_{12}H_8BrN$ , which crystallises from alcohol in large rhombic laminae, having a strong vitreous lustre, melting at  $199^\circ$ , easily soluble in boiling alcohol, and separating therefrom completely on cooling.

*Tetranitrocarbazole*,  $C_{12}H_5(NO_2)_4N$ .—This compound is obtained in four different modifications by the action of fuming nitric acid on acetyl-carbazole. They are all nearly insoluble in the ordinary solvents, but dissolve with moderate facility in glacial acetic acid at the boiling heat, and may be separated from one another by repeated fractional crystallisation.

$\alpha$ . By employing a large quantity of glacial acetic acid, the greater part of the crystalline precipitate which separates from the nitric acid solution may be dissolved, leaving only a small fraction in the form of faintly yellow needles, melting with decomposition at about  $308^\circ$ . They remain unaltered when exposed to the air or left in a vacuum, and do not lose weight when heated at  $110^\circ$ . When treated with potash, they acquire a deep yellow colour, and after some time a roseate tint.

$\beta$ . The acetic solution filtered from the crystals just described, deposits on cooling, after about 24 hours, faintly yellow tabular hexagonal crystals, which lose their lustre and transparency on exposure to the air, acquiring at the same time a lighter colour. This modification, after drying at  $105^\circ$ , does not melt even at  $320^\circ$ , and quickly acquires a bright red colour when treated with potash.

The solution from which the yellow crystals have separated, deposits, after a portion of the acetic acid has been distilled off, other crystals, always in the form of rhombic plates, having a dingy yellow colour, and melting with decomposition at about  $285^\circ$ . The crystals of  $\beta$ - and  $\gamma$ -tetranitrocarbazole, probably contain acetic acid, which they lose spontaneously on exposure to the air.

$\delta$ . The portion of the nitro-compound obtained by precipitating the acid solution with water dissolves completely in boiling glacial acetic acid; and the solution on cooling deposits, in addition to a small quantity of the  $\gamma$ -crystals, small square-based yellow prisms, which are

not altered either by exposure to the air or by heating to  $110^{\circ}$ , but decompose completely before melting.  
H. W.

**Anthramine.** By C. LIEBERMANN and A. BOLLERT (*Ber.*, **15**, 852—854).—Although anthramine cannot be produced by the action of ammonia on anthracene-monosulphonic acid, it can easily be prepared by heating at  $250^{\circ}$  a solution of anthrol in 60 times its weight of 10 per cent. aqueous ammonia.

*Anthramine hydride*,  $C_{14}H_{11}NH_2$ , obtained by treating an alcoholic solution of anthramine with sodium amalgam, crystallises in needles, which are very soluble in alcohol. The hydrochloride forms sparingly soluble needle-shaped crystals.  
W. C. W.

**Nitro- and Amido-anthraquinonesulphonic Acids.** By A. CLAUS (*Ber.*, **15**, 1514—1525).—Anthraquinonesulphonic acid (Na salt) heated with a mixture of nitric and sulphuric acids, is dissolved to a mixture of two isomeric nitro-acids. The  $\alpha$ -acid separates completely, on cooling, and is purified by recrystallisation from its solution in boiling dilute nitric acid. The  $\beta$ -acid, which remains in solution, is isolated by diluting and evaporating several times until the nitric acid is expelled, neutralising with barium carbonate, and allowing the barium salt to crystallise. From the barium salt the acid is easily obtained.

*$\alpha$ -Nitroanthraquinonesulphonic acid* crystallises in yellowish plates (m. p.  $255^{\circ}$ ); freely soluble in water and alcohol; on evaporation with nitrates it decomposes these salts with expulsion of their nitric acid. The sodium salt may be obtained directly by the long-continued action of boiling concentrated nitric acid on sodium anthraquinonesulphonate. It crystallises from boiling water, with 1 mol.  $H_2O$ , in long needles. The potassium salt crystallises from its hot aqueous solution in shining needles, which are anhydrous.

The *ammoniasalt*,  $C_{14}H_6(NO_2)O_2 \cdot SO_3NH_4 \cdot \frac{1}{2}H_2O$ , crystallises in slender needles. The *calcium salt*,  $\{C_{14}H_6(NO_2)O_2 \cdot SO_3\}_2Ca \cdot H_2O$ , crystallises in microscopic needles, which are only slightly soluble in hot water. The barium salt crystallises in anhydrous needles. The *sulphochloride*,  $C_{14}H_6(NO_2)O_2 \cdot SO_2Cl$ , is obtained by heating any of the above salts, in the anhydrous state, with phosphorus pentachloride at  $140^{\circ}$ . The chloride is almost insoluble in alcohol and in ether, but is easily soluble in hot glacial acetic acid, and crystallises from this solution on cooling in yellowish needles melting at  $194^{\circ}$ . It is not easily attacked by water, the reaction between them, with regeneration of the acid, requiring the aid of a high temperature.

$\alpha$ -Nitroanthraquinonesulphonic acid when fused with potash yields alizarin in the first instance, and on prolonged heating, purpurin or a similar colouring-matter.

*$\beta$ -Anthraquinonesulphonic acid* is freely soluble in water and in alcohol, and is left on evaporation of the solvent as a grey semi-crystalline powder melting at  $250^{\circ}$ . The salts of this acid are likewise very soluble; the sodium, potassium, and ammonium salts can only be isolated by the complete evaporation of their solutions. The *barium salt*,  $[C_{14}H_6(NO_2)O_2 \cdot SO_3]_2Ba \cdot 3\frac{1}{2}H_2O$ , crystallises from its concen-

trated aqueous solution in yellowish-red needles; the *lead salt* in small white needles containing 2 mols.  $\text{H}_2\text{O}$ . The  $\beta$ -acid yields no alizarin on fusion with potash, but a greyish-brown substance which is still under investigation.

On distillation, the calcium salts of both acids yield a product of decomposition which crystallises in shining red needles melting at  $262^\circ$ , and resembles amidoanthraquinone in its properties. In this case also, however, the authors reserve their verdict.

*Action of Reducing Agents on the Nitro-acids.*—This subject the author has studied together with Albersheim, with the following results:—

By the action of sodium-amalgam on dilute solutions of the sodium salts in the cold, the corresponding amido-acids are formed. By the further action of the amalgam in hot solution, a body resembling amidoanthraquinone is formed; and by pushing the action still further, in concentrated solutions, sodium anthracenesulphonate and hydranthracenesulphonate are formed. It is remarkable that the amido-acids are formed by the action of hydrogen sulphide on the lead salts of the nitro-acids, and this method was employed in the preparation of the  $\beta$ -amido-acid.

*$\alpha$ -Amidoanthraquinonesulphonic acid* is precipitated from the aqueous solution of its sodium salt, on addition of an acid, as a fine grey powder, which dries to a bronze coloured powder with a metallic lustre. It is only slightly soluble in alcohol and in ether. Heated to  $110^\circ$ , it loses 1 mol. water. Its salts are of a deep red colour, and those which are soluble in water are capable of application for dyeing purposes.

The *sodium salt*,  $\text{C}_{14}\text{H}_6(\text{NH}_2)\text{O}_2\cdot\text{SO}_3\cdot\text{Na}\cdot 1\frac{1}{2}\text{H}_2\text{O}$ , crystallises from its solution in hot alcohol, in groups of red needles; the *calcium salt*,  $[\text{C}_{14}\text{H}_6(\text{NH}_2)\text{O}_2\cdot\text{SO}_3]_2\text{Ca}\cdot 5\text{H}_2\text{O}$ , from its aqueous solution in shining red needles; the barium salt with  $3\frac{1}{2}$  mols.  $\text{H}_2\text{O}$  also in red needles; the lead salt with  $2\frac{1}{2}$  mols.  $\text{H}_2\text{O}$ ; the copper salt with  $7\frac{1}{2}$  mols.  $\text{H}_2\text{O}$  in yellowish-red needles.

*$\beta$ -Amidoanthraquinonesulphonic acid* is obtained as a reddish-brown resinous mass; both the acid and its salts are extremely soluble in water, forming red solutions which exceed those of the  $\alpha$ -acid in tinctorial power.

*Action of sulphuric acid on the nitro-acids.*—This has been investigated by the author in collaboration with Engelsing, with the following results:—

$\alpha$ -Nitroanthraquinonesulphonic enters into reaction with sulphuric acid at  $198^\circ$ , a considerable evolution of sulphurous anhydride taking place. If the temperature is maintained at this point the decomposition is limited to the formation of two bodies, one having a violet, the other a magenta-red colour; these bodies are held by the author to be derivatives of a dihydroxynitroanthraquinonesulphonic acid.

The blue compound was found in effect to be entirely converted into the latter red body by the action of sulphuric acid in excess at  $198^\circ$ . The ethereal character of the former compound is shown by its conversion on boiling with dilute potash, into dihydroxyanthraquinonesulphonic acid. This acid was obtained as a reddish powder on

evaporating its aqueous solution. It is soluble in hot alcohol, separates on cooling as a crystalline powder, which on drying acquires a green metallic lustre. The authors are engaged in the completion of these investigations. C. F. C.

**An Isomeric Dichlorocamphor.** By P. CAZENEUVE (*Compt. rend.*, **94**, 1360—1362).—A dichlorocamphor,  $C_{10}H_{14}Cl_2O$ , has already been obtained by the author by passing chlorine into a solution of camphor in absolute alcohol, decomposing the viscous liquid thus obtained with water, and dissolving the product in alcohol ( $93^\circ$ ); on cooling the solution in a freezing mixture, the dichlorocamphor is deposited in a crystalline state. By precipitating the mother-liquor with water, pressing the butyraceous product on a slab of plaster to remove water and an aromatic oil, washing the residue with dilute alcohol, and crystallising from the smallest possible quantity of absolute alcohol by means of a refrigerating mixture, an isomeride of the above is obtained. It is exceedingly soluble in alcohol, from which it crystallises with difficulty; it is also very soluble in ether and chloroform, liquefying even in their vapours. It liquefies in contact with chloral hydrate, in which it differs from its isomeride, which the author calls normal dichlorocamphor. It softens at  $70^\circ$  and melts at  $77^\circ$ , whilst the normal compound melts at  $96^\circ$ . Even when not exposed to sunlight, the isomeric chlorocamphor evolves acid vapours.

Its solution in alcohol has the rotatory power  $[\alpha]_D = +57.4^\circ$ ; in chloroform  $[\alpha]_D = +60.6^\circ$ ; for both liquids the normal compound  $[\alpha]_D = 57.3^\circ$ . L. T. O'S.

**Curcumin.** By C. L. JACKSON and A. E. MENKE (*Amer. Chem. J.*, **4**, 77—91).—This substance, the yellow colouring matter of turmeric, has been examined by several chemists, whose experiments have led to the conclusion that its formula is either  $C_{10}H_{10}O_3$  or  $C_{16}H_{16}O_4$ ; that it melts at  $172^\circ$ ; forms red-brown salts with alkalis; is converted by boric or sulphuric acid into rosocyanine; by reduction with zinc-dust into an oily body; by oxidation into oxalic or terephthalic acid; and by fusion with potash, into protocathechuic acid. The experiments of Jackson and Menke have however led to results differing in many respects from those above detailed, which were probably obtained with impure preparations.

The curcumin used in the authors' experiments was prepared by treating ground turmeric root (Bengal or Madras) with light petroleum to remove turmeric oil, and then with ether, which dissolves the curcumin together with a large quantity of resin; and it was finally purified by crystallisation from alcohol. The quantity of curcumin thus obtained was only 0.3 per cent. of the root; the total quantity contained in the root is however much larger, as a considerable amount remains mixed with the resinous impurities, and some also in the oil.

Curcumin thus prepared crystallises from alcohol in stout needles, appearing on microscopic examination to be made up of well-formed prisms with square ends, or in spindle-shaped crystals often arranged in radiate groups. It has an orange to yellow colour, according to the size



of the crystals, with a beautiful blue reflex; its solution in ether exhibits a strong green fluorescence. It is inodorous when pure; melts at  $178^{\circ}$ , apparently with decomposition. It is nearly insoluble in water, somewhat soluble in cold, more readily in hot ethyl and methyl alcohols, more soluble in glacial acetic acid, less in ether, very slightly in benzene and carbon bisulphide, and all but insoluble in light petroleum. Strong sulphuric acid dissolves it with a fine reddish-purple colour, gradually changing to black from charring; the same effect is produced, though more slowly, by strong hydrochloric acid. Curcumin dissolves readily in alkalis and alkaline carbonates, to a slight extent also when boiled with water and calcium carbonate. Its ammoniacal solution gives off ammonia when boiled, and deposits unaltered curcumin. Baryta-water converts it into a blackish-red powder, but lime-water gives a red solution like that obtained with calcium carbonate. Curcumin is not affected by acid sodium sulphite.

Pure curcumin gives, as the mean of several analyses, 68.30 per cent. carbon and 5.63 hydrogen, leading to the formula  $C_{14}H_{14}O_4$ , which requires 68.29 C, 5.69 H, and 26.02 O; and this formula has been confirmed by the analysis of several derivatives.

The *dipotassium salt*,  $C_{14}H_{12}K_2O_4$ , prepared by adding a large excess of strong alcoholic potash to a hot alcoholic solution of curcumin, separates in flame-coloured crystals, and may be precipitated from weaker solutions by addition of ether. When first formed, it consists of globular radiate groups of flame-coloured needles, but assumes a deep claret colour on drying. It is freely soluble in water, somewhat less so in alcohol, and nearly insoluble in ether. The alcoholic solution assumes a magenta colour on exposure to the air, probably from oxidation. The *monopotassium salt*,  $C_{14}H_{13}KO_4$ , is formed on adding an excess of potassium carbonate to a hot solution of curcumin in absolute alcohol, and separates on addition of ether in crimson-black flocks, having the lustre of rosaniline and a somewhat blacker green colour. It is very soluble in water and in alcohol. It may also be made by adding an excess of curcumin to the dipotassium salt, or by adding potash, not in excess, to curcumin suspended in alcohol. The *calcium salt*, obtained by precipitation from the monopotassium salt, is flame-coloured, and slightly soluble in water. The *zinc salt* appears to be soluble, the *barium salt* insoluble; the *silver salt* appears to be very unstable.

The fact that only one atom of the hydrogen in curcumin can be replaced by the potassium in potassic carbonate, seems to indicate the existence of one, and only one, carboxyl-group in its molecule, whilst the replacement of a second H-atom by the action of an excess of potassium hydroxide points to the existence of a hydroxyl-group, probably a phenolic hydroxyl, and leads to the inference that curcumin is a diatomic monobasic acid.

*Parabromobenzyl-curcumin*,  $C_{14}H_{13}(C_7H_4Br)O_3$ , is formed by adding an excess of *p*-bromobenzyl bromide to an alcoholic solution of monopotassium-curcumin, and separates in pale yellow crystals, which, after purification, melt at  $76-78^{\circ}$ . It is more soluble in glacial acetic acid than in alcohol, but crystallises better from the latter; readily soluble in ether and in benzene, slightly in carbon sulphide, nearly insoluble in light petroleum; it is not attacked by potassium carbonate, but

dissolves in caustic potash, though without the red colour characteristic of curcumin.

*Oxidation of Curcumin.*—By oxidation with chromic acid mixture, curcumin is wholly converted into acetic acid and carbonic anhydride, not a trace of terephthalic acid having been found in the product; by incomplete oxidation with potassium permanganate in alkaline solution, it yields vanillin,  $C_8H_8O_3 = C_6H_3(CHO)(OMe)(OH)$ . Hence, and from the fact previously established that curcumin contains a carboxyl-group, the authors infer that its constitutional formula is  $C_6H_3(CH.C_5H_5.COOH)(OMe)(OH)$ . The structure of the group  $C_5H_5$  will be made the subject of further investigation. H. W.

**Is Gelsemic Acid Identical with Aesculin?** **Observations on the Preparation, Properties, and Recovery when absorbed of the Important Constituents of Gelsemium sempervirens, and on Gelsemium Poisoning.** By T. G. WORMLEY (*Pharm. J. Trans.* [3], 13, 106—108).—Gelsemic acid was prepared by extracting the acidulated extract of the root with ether; and from the extracted liquid gelsemine was obtained by neutralisation and agitation with ether. Comparison of the properties, chemical and physical, shows that gelsemic acid is not identical with aesculin; the solubility of gelsemic acid in water is 1 in 2912 (18—24°), in ether 1 in 330. Results with various reagents are fully described, and also the effect produced on animals, the fatal period being, as found in a few cases of poisoning, 1—8 hours. No antidote is known; electricity and hypodermic injection of morphia have proved beneficial. In applying the tests for gelsemic acid to the ether residue from the acid solution, it should be remembered that although the reaction of the nitric acid and ammonia test is common to gelsemic acid and aesculin, yet when obtained from an ether extract it is characteristic of the former, as the latter is not extracted by ether. The principal tests are as follows: sulphuric acid dissolves gelsemic acid with a yellow colour, no change being produced by heat; if a drop of aqueous ammonia be added to the solution, a dirty white cloud of minute needles is formed. Nitric acid dissolves gelsemic acid with a yellow colour, and the addition of ammonia in excess produces a deep red; this test detects  $\frac{1}{5000}$  grain. With gelsemine, nitric acid produces a brown-green, changing to deep green; this serves to distinguish the alkaloid from strychnine, &c. The reaction with sulphuric acid and potassium dichromate somewhat resembles that of strychnine. E. W. P.

**Pyridine-betaïne.** By E. v. GERICHTEN (*Ber.*, 15, 1251—1254).—The author has described a base, dibromapophylline,  $C_{14}H_{10}Br_2N_2O_4$ , a bye-product of narcotine, which when heated with hydrochloric acid yields methyl-dibromopyridyl-ammonium chloride. As the former possesses a molecular weight double of that indicated by theory for dibromopyridine-betaïne, the author to establish the identity of these compounds has prepared pyridine-betaïne and its dibromo-derivative synthetically. Pyridine-betaïne hydrochloride is obtained by heating pyridine and monochloroacetic acid in molecular proportions; a dark

golden syrup is formed which on further heating solidifies to a mass of white needles; on crystallising these from water the salt is obtained pure in the form of large glistening rhombic tables. The reaction is

as follows:  $C_5H_5N + CH_2Cl.COOH = C_5H_5N \begin{matrix} CH_2 \\ \diagup \quad \diagdown \\ -O- \end{matrix} CO, HCl$ . The

salt is sparingly soluble in cold water, alcohol, and ether; it softens at  $190^\circ$ , and at  $202-205^\circ$  melts to a brown liquid, with violent evolution of carbonic anhydride and methyl chloride, according to the

reaction  $C_5H_5N \begin{matrix} CH_2 \\ \diagup \quad \diagdown \\ -O- \end{matrix} CO, HCl = CO_2 + MeCl + C_5H_5N$ . Its platino-

chloride forms orange-red, tough crystals, soluble in cold water, insoluble in alcohol. The free base was obtained by digesting the hydrochloride with freshly precipitated silver oxide; it crystallises in glistening rhombic tables containing 1 mol. of water. It is easily soluble in water, insoluble in ether. At  $150^\circ$  it melts partially, with evolution of gas, and subsequent formation of a carbonaceous mass. The aqueous solution of the betaine hydrochloride is coloured deep blue by sodium amalgam; the colour disappears on shaking the solution in the air, but is renewed on heating. The author, however, did not examine the nature of the reaction. On heating dibromopyridine with monochloroacetic acid, a partial reaction takes place after some time, with formation of dibromopyridine-betaine hydrochloride. This salt begins to decompose at  $184^\circ$ , and at  $193^\circ$  melts into a black liquid, with evolution of gas. The platinochloride crystallises in large brown glistening prisms. The researches are insufficient to establish the identity of dibromapophylline with dibromopyridine-betaine.

On heating quinoline and monochloroacetic acid in molecular proportions, a brown syrup is obtained, which gives a platinochloride crystallising in star-like orange-golden needles. V. H. V.

**Tetrabromoquinoline and Di-iodoquinoline.** By A. CLAUS and E. ISEL (*Ber.*, 15, 820—825).—Quinoline dissolved in carbon bisulphide, when acted upon by bromine dissolved in the same solvent, yields a resinous product, from which quinoline hydrobromide and a small quantity of tetrabromoquinoline can be obtained.

*Tetrabromoquinoline*,  $C_9H_3Br_4N$ , is insoluble in water, but soluble in alcohol and carbon bisulphide. From the former, it crystallises in long needles, and from the latter in short thick yellowish prisms melting at  $119^\circ$ . It sublimes without decomposition; has no basic properties; is dissolved without action by concentrated sulphuric acid; withstands the action of aqueous and alcoholic potash. On heating it with concentrated nitric acid, bromine is evolved, and a nitro-compound (m. p.  $264-266^\circ$ ) is obtained.

*Dibromotetrahydroquinoline*,  $C_9H_7Br_2N$ , is obtained by the action of sodium amalgam on an alcoholic solution of tetrabromoquinoline. This compound is insoluble in water, but soluble in the other ordinary solvents; crystallises in tabular colourless crystals (m. p.  $65-66^\circ$ ). It is volatile in steam, and exhibits basic properties. The following salts have been prepared:—

The *sulphate*,  $C_9H_9Br_2N.H_2SO_4$ , forms white leaflets; the *oxalate* forms tabular colourless crystals (m. p.  $171^\circ$ ); the *nitrate* crystallises in reddish columnar crystals (m. p.  $189^\circ$ ); the *hydrochloride* crystallises from water in reddish stellate groups of needles (m. p.  $74-75^\circ$ ); the *platinochloride*,  $(C_9H_9Br_2N.HCl)_2PtCl_4 + 2H_2O$ , is obtained as a light-yellow crystalline precipitate.

*Di-iodoquinoline*,  $C_9H_7I_2N$ , is formed by the action of a solution of iodine in carbon bisulphide on a similar solution of quinoline. It is a direct addition-product, forms dark-green lustrous needles melting at  $90^\circ$ , and is easily soluble in alcohol, ether, &c. It possesses basic properties, and forms a platinochloride. By the action of sodium amalgam the iodine is removed, and diquinoline appears to be formed (*Ber.*, **14**, 1939). Carbon bisulphide is without action on quinoline, even at high temperatures; sulphur, however, acts on it at high temperatures, hydrogen sulphide being evolved, and a reddish-brown mass obtained, which is insoluble in water, but soluble in alcohol, &c.; this exhibits basic properties, and forms a dark-red platinochloride.

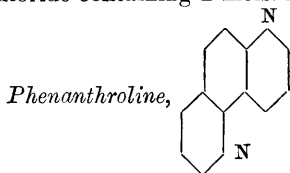
P. P. B.

**Quinoline Derivatives.** By Z. H. SKRAUP (*Ber.*, **15**, 893—898).—The following table shows that the metatoluquinoline derivatives melt or boil at a higher temperature than the corresponding ortho- and para-compounds. :—

	Ortho.	Para.	Meta.
Toluquinoline boils at .....	$236^\circ$	$245^\circ$	$252^\circ$
Hydroxyquinoline melts at ..	$75$ (b. p. $258^\circ$ )	$190$	$238$ (circa)
Quinolinebenzocarboxylic acid melts at .....	$187$	$291$	above $350^\circ$

The hydroxyquinolines are soluble in hot water and in alcohol. The ortho-compound is also soluble in benzene, and is volatile in a current of steam. The platinum salt of orthhydroxyquinoline forms golden-yellow needles; the corresponding para- and meta-compounds form reddish-yellow precipitates. Ferric chloride gives a green coloration with orthhydroxyquinoline, a faint red with meta-, and no coloration with parhydroxyquinoline.

Parabenzochloroquinoline melts at  $264^\circ$ ; parachloroquinoline, like the three hydroxyquinolines and toluquinolines, yields a platinochloride containing 2 mols.  $H_2O$ .



obtained by the action of glycerol and

sulphuric acid on metadiamidobenzene, crystallises in transparent plates (m. p.  $79^\circ$ ), soluble in alcohol. The crystals unite with water, forming the hydrate,  $C_{12}H_8N_2 + 2H_2O$ , which melts at  $66^\circ$ . On the addition of bromine to the aqueous solution of the hydrochloride, a yellow crystalline addition-product,  $C_{12}H_8N_2Br_2$ , is obtained, which is

not decomposed by boiling water, but is converted by hot alcohol into a compound crystallising in beautiful red plates, probably  $C_{12}H_8N_2Br_2 + C_{12}H_6N_2BrH$ .

When phenanthroline is heated in closed tubes with bromine and water,  $C_{12}H_8Br_2N_2$  is formed. On reduction with tin and hydrochloric acid, a non-crystalline product,  $C_{12}H_{14}N_2$  or  $C_{12}H_{16}N_2$ , is obtained, and on oxidation with potassium permanganate, *dipyridyldicarboxylic acid*,  $C_{12}H_8N_2O_4 + 2H_2O$ , is produced. This acid crystallises in prisms, which melt at  $217^\circ$ , but when heated at  $200^\circ$  for some time lose carbonic anhydride and form *dipyridylmonocarboxylic acid* (m. p.  $179^\circ$ ). Paradiamidobenzene also yields a new base,  $C_{12}H_8N_2$  (m. p.  $173^\circ$ ).

The author finds that salts of the amido-compounds may be used instead of the free bases in the glycerol quinoline reactions.

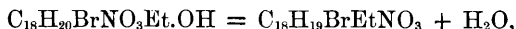
W. C. W.

**Addition-products of the Bases obtained from Quinoline and the Alkyl Chlorides and Iodides.** By W. LA COSTE (*Ber.*, **15**, 809—811).—This is a reply to the criticisms of Claus (*Ber.*, **15**, 475) on a former communication of the author (*ibid.*, 186). P. P. B.

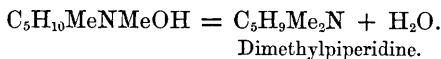
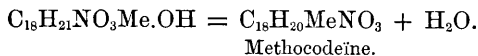
**Contribution to the Knowledge of the Alkaloids of the Papaveraceæ.** By J. F. EYKMAN (*Pharm. J. Trans.* [3], **13**, 87).—Of the alkaloids of the *Papaveraceæ* but little is known, except those contained in *P. somniferum*. Of the remaining papaveraceous plants, *Sanguinaria* and *Chelidonium* have been the most studied. In a Japanese plant, *Macleya cordata* (Japanese, Tachiobaku), the author has found a new alkaloid, *Macleylene*. The laborious method of extraction and purification is fully described. The alkaloid melts at  $200.5\text{--}201^\circ$ , and is almost insoluble in water and alkalis. Its composition is  $C_{20}H_{19}NO_5$ . The chemical properties of macleylene closely resemble those ascribed to protopine in opium (Hesse), but as yet the identity is not fully proved, although it is highly probable. E. W. P.

**Morphine and Codeïne.** By E. v. GERICHTEN and H. SCHRÖTTER (*Ber.*, **15**, 1484—1488).—The authors having obtained phenanthrene from morphine by distilling it with zinc-dust, and being desirous of establishing the reaction as one of simple direct transformation, and the hydrocarbon therefore as the "dominant" of the morphine molecule, have applied to the solution of this point a reaction suggested by Hofmann's researches on the pyridine bases (*ibid.*, **14**, 494, &c.), as follows:—

Bromocodeïne was converted into the ethiodide, and this into the corresponding ammonium base. The latter on boiling was transformed with loss of water into the tertiary base, orthobromocodeïne, according to the equation—



analogous to the decompositions of the homologous methyl base (Grimaux, *ibid.*, **14**, 2693), and of dimethylpiperyl-ammonium hydroxide (Hofmann, *loc. cit.*), as represented by their respective equations—



The resulting tertiary base, ethobromocodeine, was converted into the methiodide, and the corresponding ammonium base heated for some time on the water-bath. It was found to be thus resolved into a mixture of bases, trimethylamine and others, and a non-nitrogenous body,  $\text{C}_{15}\text{H}_9\text{BrO}_2$ , obtained in the crystalline state (m. p.  $121^\circ$ ). On oxidation with chromic acid in acetic solution, this body yielded a quinone closely resembling phenanthraquinone.

Similar results were obtained with codeine itself. The products of resolution of the ammonium base were chiefly methylethylpropylamine and a non-nitrogenous body,  $\text{C}_{15}\text{H}_{10}\text{O}_3$ , obtained in colourless needles melting at  $65^\circ$ , and yielding phenanthrene on distillation with zinc-dust. The resolution of the base may be thus formulated:—



The authors withhold the more complete discussion of these results in their bearings on the constitution of morphine until that of the phenanthrene derivative is definitely established. C. F. C.

**Remarkable Behaviour of Quinine Hydrochloride.** By VULPIUS (*Ann. Pharm.* [3], 20, 361).—If silver nitrate be cautiously added to quinine hydrochloride, both in dilute solution, so as to avoid excess of the former, no precipitate of silver chloride is formed. This may arise from the formation of a soluble double chloride. Some other alkaloids appear to behave in the same manner, but morphine does not. E. W. P.

**Cinchona Alkaloids.** By O. HESSE (*Ber.*, 15, 854—859).—*Hydroquinidine*,  $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_2 + 2\frac{1}{2}\text{H}_2\text{O}$ , contained in the mother-liquors from quinidine sulphate, crystallises in efflorescent prisms (m. p.  $168^\circ$ ) which are soluble in hot alcohol and chloroform. A solution of the base in dilute sulphuric acid exhibits a blue fluorescence. On addition of chlorine-water and ammonia in excess to this solution, a dark-green coloration is produced. The neutral sulphate resembles quinidine sulphate in appearance, but is distinguished from the latter substance by its greater stability when treated with potassium permanganate.

*Hydroquinine*,  $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_2$  (m. p.  $168^\circ$ ), is soluble in alcohol and ether. The sulphuric acid solution exhibits a blue fluorescence, and yields a white precipitate with ammonia. It resembles quinine in its reaction with chlorine and ammonia, but differs from quinine in its power of resisting the action of potassium permanganate in acid solutions. The following salts were prepared:  $(\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_2)_2\text{C}_4\text{H}_6\text{O}_6 + \text{H}_2\text{O}$ , colourless prisms, slightly more soluble in cold water than quinine tartrate;  $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_2\cdot\text{PtCl}_6\text{H}_2 + 2\text{H}_2\text{O}$ ; and  $(\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_2)_2\text{H}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$ , colourless needles, sparingly soluble in cold water. This salt

has a somewhat feeble levogyrate action on polarised light than quinine sulphate.

*Cincholine* is prepared from the first mother-liquor obtained in the manufacture of quinine sulphate. After adding potassium-sodium tartrate, potassium thiocyanate is then dropped into the mixture until no further precipitate is produced. The alkaloids in the filtrate are set free by addition of soda, and extracted with ether. The residue which remains on evaporating the extract is repeatedly boiled with water, and the volatile alkaloids are collected in dilute hydrochloric acid. The aqueous solution is evaporated to dryness, mixed with soda, and extracted with ether. The ethereal solution is washed with water and mixed with an ethereal solution of oxalic acid, which precipitates cincholine oxalate.

Cincholine is a pale-yellow oil, lighter than water. It dissolves readily in ether, alcohol, chloroform, and hydrochloric acid.

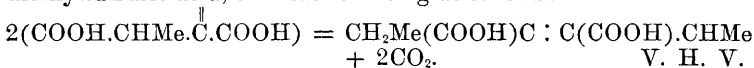
W. C. W.

**Pyrocinchonic Acid and its Formation from Oil of Turpentine.** By W. ROSE (Ber., 15, 1318—1322).—The author in a former communication has described an acid of the composition of acrylic acid which is obtained by the oxidation of oil of turpentine and as a bye-product in the preparation of terebic acid. If the mother-liquor from the terebic acid is distilled, a golden oil passes over which crystallises in the receiver; after purification, it forms glistening leaflets (m. p. 96°, b. p. 223°), subliming in the air, of composition  $C_8H_6O_3$ . Its aqueous solution is strongly acid and decomposes carbonates; the calcium salt,  $C_8H_6O_4Ca$ , and barium salt crystallise in needles; the silver salt,  $C_8H_6O_4Ag_2$ , is a bulky, sparingly soluble precipitate which on heating decomposes thus:  $C_8H_6O_4Ag_2 = C_8H_6O_3 + Ag_2 + O$ . With ferric chloride, a solution of the sodium salt gives a dark-red coloration, and with lead and mercuric chlorides, bulky crystalline precipitates. On oxidation with chromic mixture the substance yields acetic acid and carbonic anhydride, thus:  $C_8H_6O_3 + O_4 + H_2O = 2MeCOOH + 2CO_2$ . The substance in question is probably the anhydride of a dibasic acid,  $C_8H_6O_4$ , and its lactonic nature (spontaneous formation of an anhydride), taken in connection with the

formation of acetic acid on oxidation, point to a formula  $\begin{array}{c} \text{MeC.CO} \\ \parallel \\ \text{MeC.CO} \end{array} \text{O}$ ,

which is that of an anhydride of dimethylfumaric acid.

This substance is probably identical with Weidel's pyrocinchonic acid, which is derived from cinchomeronic acid, thus:  $C_7H_5NO_4 + H_2O + H_2 = NH_3 + C_7H_6O_5$  and  $C_7H_6O_5 = C_8H_6O_3 + CO_2$ . It is also probable that the imperfectly described metacamphoric acid is, considering the relation of camphor to turpentine, impure dimethylfumaric anhydride (pyrocinchonic acid). The xeronic acid of Pittig,  $C_8H_{12}O_4$ , is an analogue of dimethylfumaric acid, possessing similar properties, and, as it is formed from citraconic acid, it is probably diethylfumaric acid, the reaction being as follows:—



V. H. V.

**Piperylhdyrazine.** By L. KNORR (*Ber.*, 15, 859—861).—On reduction with zinc-dust and acetic acid, nitrosopiperidine is converted into piperylhdyrazine; small quantities of piperidine and ammonia are also formed. (If sodium-amalgam is used instead of zinc-dust and acetic acid, piperidine and ammonia are the chief products of the reaction.) The crude product is mixed with an excess of alkali and distilled. The distillate deposits crystals of dipiperyltetrazone, which are removed by filtration. The filtrate is neutralised with hydrochloric acid, evaporated to dryness, and dissolved in hot alcohol. From this solution needle-shaped crystals of *piperylhdyrazine hydrochloride*,  $C_5H_{10}N.NH_2.HCl$ , are deposited. The crystals (m. p.  $162^\circ$ ) dissolve in water and in hot alcohol. The free base is an oily liquid boiling at  $145^\circ$ . By the action of mercuric oxide on its ethereal solution it is converted into the tetrazone,  $C_{10}H_{20}N_4$ , melting at  $45^\circ$ . This compound is almost insoluble in water; it dissolves in acids, but is decomposed when heat is applied to the acid solution. W. C. W.

**Action of Acids on Pilocarpine.** By P. CHASTAING (*Compt. rend.*, 94, 968—970).—Fuming nitric acid transforms pilocarpine into nitrate of jaborandine,  $C_{10}H_{12}N_2O_3.HNO_3$ . Hydrochloric acid, by acting on pilocarpine in presence of the oxygen of the air, gives rise to hydrochloride of jaborandine, and also to jaborine in small quantity. R. R.

**Substances analogous to the Ptomaines in Digested Albuminoid Matters.** By J. BÉCHAMP (*Compt. rend.*, 94, 973—975).—The paper describes investigations which show that certain normal products of the organism and of the digestion of albuminoid bodies, contain substances which have the characters of ptomaines, and in their chemical reactions closely resemble certain very poisonous alkaloids. These substances are, however, physiologically harmless in their effects on frogs. R. R.

**The Mechanism of Putrid Fermentation of Proteid Substances.** By A. GAUTIER and A. ETARD (*Compt. rend.*, 94, 1357—1360).—The authors have observed the different stages of putrefaction of the flesh of the ox, horse, and fish exposed to the heat of summer in large oak barrels or glass vessels.

At first the ox or horse flesh had an acid reaction and no smell. After some days, even when protected from vibrios, the flesh emitted an acid odour; and a clear, almost colourless syrupy liquid exuded from it, resembling a thick serum, and containing per litre 21—22 grams albumin coagulable by heat, and a very small quantity of casein. This liquid appears to be formed by an incipient digestion of the flesh, due to a fermentation peculiar to itself. At the same time, lactic and butyric fermentation set in under the influence of large bacilli with three or four joints, and bacteria and mobile granulations.

During the process, gases are evolved containing at different stages carbonic anhydride, nitrogen, hydrogen, sulphuretted hydrogen, and phosphoretted hydrogen, but no trace of hydrocarbons was detected at any stage.



At first principally carbonic anhydride and hydrogen are evolved, attaining almost equal proportions between the 6th and 11th days, which suggests the decomposition of some carbohydrate into lactic and butyric acids, thus:  $2C_6H_{12}O_6 = 2C_3H_6O_3 + C_4H_8O_2 + 2CO_2 + 2H_2$ . Ordinary lactic acid (not sarcolactic acid), normal butyric acid and homologues, and some acids which reduce silver salts and form sparingly soluble zinc salts, are found in the liquid. This phenomenon precedes the true putrid fermentation, which begins towards the 4th or 5th day, with evolution of nitrogen, the large bacilli and bacteria disappearing at the same time, whilst very small bacilli take their place. The albuminoid molecule is now attacked, carbonic anhydride and ammonia are evolved, and the reaction becomes alkaline; the proteid molecule is partially decomposed, with evolution of nitrogen, sulphuretted hydrogen, and phosphoretted hydrogen, but the greater portion forms *leucines* and *leuceines*, together with smaller quantities of phenol, skatole, indole, and, according to the authors' researches, carbylamine and ptomaines.

After a certain time, even in the middle of summer, the putrefactive action ceased simultaneously with the evolution of gas, the flesh preserving its colour and form, and seeming to have reached a non-putrescible state, even after all the products of the fermentation had been separated and it was again submitted to the action of air and water.

That the acid fermentation is not necessary to putrefaction, and does not affect the albuminoid molecule, is more clearly shown in the putrefaction of fish, in which case the amount of hydrogen evolved and butyric acid formed is very small, the latter being neutralised by the ammonia and methylamines which are accompanied by sulphuretted and phosphoretted hydrogen. As in the case of beef, the evolution of gas ceases after some time, but, on the contrary, the molecular decomposition continues. The liquid at first contains 21 grams albumin per litre, but after some months this disappears; neither does it contain casein, but it contains substances soluble in alcohol, and very similar in colour and smell to those obtained from flesh. On heating the liquid and evaporating it in a vacuum, crystals are obtained which appear to consist of leucine, leuceine, ammoniacal salts, and putrefactive alkaloids.

L. T. O'S.

**Urochloralic Acid.** By E. KÜLZ (*Ber.*, **15**, 1538).—The recent appearance of a paper by v. Mering (*ibid.*, 1019) on the reduction processes of the animal body, in which he ignores the author's published work (*ibid.*, **14**, 2291) on the preparation of urochloralic acid from the urine of dogs under treatment with chloral hydrate, has evoked from the author this reproduction in full of certain passages in his original paper, and the expression of the hope that v. Mering may be induced to duly recognise his contributions to the subject.

C. F. C.

## Physiological Chemistry.

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### Influence of Peptones on the Diastatic Action of Saliva.

By R. H. CHITTENDEN and J. S. ELY (*Amer. Chem. J.*, **4**, 107—123).

—Human mixed saliva in presence of an equal volume of artificial gastric juice containing 0.05 p.c. hydrochloric acid, can form, out of a given quantity of starch, a much larger amount of sugar than that which would be produced by the action of the same quantity of saliva alone under a like degree of dilution; this being the more remarkable when it is remembered that the same percentage of acid by itself greatly retards the diastatic action. Many of the digestive processes of the body appear indeed to be dependent, for their full action, on the stimulating or other influence caused by the mere presence of many of the digestive products, in a greater degree than has hitherto been supposed. It is true that several of the products of digestion, when present in the digestive mixture in excess—especially sugar in the case of salivary digestion and peptones in gastric digestion—actually retard the digestive process; but in the normal body under ordinary circumstances, all conditions are favourable for a rapid absorption of the digestive products, and thus any excessive accumulation is prevented.

Schmidt Mülheim, in his recent study of proteid digestion (*Du Bois Reymond's Archiv. f. Physiologie*, 1879, 39), found that in the case of dogs, the quantity of peptones present in the stomach was practically the same at all times during digestion; thus 1, 4, and 6 hours after a dog had been fed with 0.1 gram of albumin, the stomach was found to contain 3.08, 3.31, and 2.91 grams respectively of peptones, indicating apparently that, after the formation of a definite quantity of the digestive products, the transportation of these bodies keeps pace with the digestion. Again there are no facts to warrant the belief that the products of one digestive process necessarily hinder the action of some other allied ferment; indeed it is commonly understood that any accumulation of the digestive products simply hinders the action of the particular ferment to whose action they are due, by clogging the digestive fluid. There is therefore nothing inconsistent in the statement that the products of one digestion may act as a stimulant to some other digestive process.

The experiments described in the present paper have established the following facts:—

1. *Peptones, a product of gastric digestion, exercise a decided influence on salivary digestion, stimulating the ferment to increased action, particularly in presence of acid, which by itself completely prevents the conversion of starch into sugar.*

2. *The inorganic salts contained in the peptones play but an unimportant part in the stimulating action noticed in an alkaline solution containing 0.3, 0.15, and 0.05 p.c. sodium carbonate.*

H. W.

**Microzymas of the Gastric Glands, and their Digestive Power.** Answer to the question "Does the Stomach Digest Itself" ? By A. BÉCHAMP (*Compt. rend.*, **94**, 879—883).—This paper describes the methods by which the author succeeded in isolating the organised agent which constitutes the active organic matter of the gastric juice in the glands of the stomach. It is formed of isolated microzymas and of microzymas still united as granular nuclei of the glandular cells. In presence of hydrochloric acid, this matter is capable of dissolving fibrin, casein, musculin, &c., in the same manner as the gastric juice. It is constituted of a special modification of albuminoid matter.

As, under the influence of hydrochloric acid at the physiological temperature, the mucus of the stomach would disappear except the microzymas, the stomach is itself digested by its microzymas, but in the action of the glands their cells become turbid, that is to say, there is organisation, multiplication of microzymas, formation of new cells to replace those which disappear. If therefore the gland does not seem to dissolve, it is because production is greater than consumption. R. R.

**Gastric Microzymas and Pepsin.** By A. BÉCHAMP (*Compt. rend.*, **94**, 970—973).—In reference to a statement of Gautier's affirming that "insoluble pepsin is gradually transformed by pure water into soluble pepsin," the author reiterates his observations concerning the organised bodies to which he has given the name of *microzymas*, and which have since been everywhere observed, but in Germany have been called *micrococcus*. As organisms these are necessarily insoluble. They are capable, under certain conditions, of evolving *vibriones* by passing through the state of associated microzymas to which the name of *torula* has been given. Their functions in the various organs are diverse, as they may produce bacteria or even tissues. In spite of their extreme smallness, they produce pepsin by chemical actions of a vital kind, and contain it, just as the liver produces and contains bile, glucose, &c. The pepsin thus secreted manifests its chemical activity on albuminoid substances only in a suitably acidulated medium.

R. R.

**Papayotin.** By E. GEISSLER (*Arch. Pharm.* [3], **20**, 457).—Whilst pepsin is capable of dissolving a hundred times its own weight of coagulated albumin, papayotin can only bring into solution at the most 28 times its weight.

E. W. P.

**Pancreatic Digestion.** By E. DUCLAUX (*Compt. rend.*, **94**, 808—810).—The action of the pancreatic secretion was examined by the author by introducing fragments of the pancreas itself into solutions in such a manner as to prevent access of the ferment germs usually present in the pancreatic juice. A small fragment of the pancreas caused the liquefaction of starch-paste and the disappearance of the starch granules, with the exception of their exterior covering, which is formed of cellulose. A milligram of pancreas tissue rendered 10 c.c. of milk transparent in a few hours, and then it was not precipitable either by acids or by potassium ferrocyanide. The action of

the pancreas on raw meat consisted of a solution of the interfibrillary substance, so that the elementary fibrillæ became separated, and this was followed by the gradual transformation of the whole of the meat into a pulp, without, however, a complete solution taking place. Fragments of pancreas which had remained for a year were removed with their original forms and dimensions from the vessels in which they had produced these transformations. This shows that, contrary to the received opinions, the pancreas does not digest itself.

R. R.

**Pancreatic Albuminoids.** By J. BÉCHAMP (*Compt. rend.*, **94**, 883—886).—The experiments described in this paper tend to establish the difference between the gastric and pancreatic digestions. In the former the rotatory power of the transformed matter is but little lessened, or remains unchanged, or is increased, whilst in the latter it is always enormously lowered.

R. R.

**Digestion of Fatty and Celluloïd Matters.** By E. DUCLAUX (*Compt. rend.*, **94**, 976—980).—The author considers that the fatty matters of food are completely emulsified by the pancreatic juice and are then directly absorbed by the blood. Celluloïd substances are incapable of transformation by the gastric and pancreatic diastases, and must therefore be rendered soluble by the action of diastases contained in the intestinal fluids. Some observations on the condition of grains of barley taken from the crop of birds are described. In these the amylaceous masses were found without envelopes, floating in a liquid containing multitudes of minute organisms analogous to the amylobacteria which are known to act as ferments on cellulose.

R. R.

**Intestinal Digestion.** By E. DUCLAUX (*Compt. rend.*, **94**, 877—879).—In the intestinal digestion, certain ferments play a part by producing diastases which superimpose their own digestive actions on those set up by the diastases of the organism. Neither the diastases of ferments nor those of the organism ever cause a disengagement of gas, and the carbonic acid and hydrogenated gases formed in the intestines must be attributed to the microbes living therein.

R. R.

**Digestive Fluids and Digestion in Horses.** By ELLENBERGER and HOFMEISTER (*Bied. Centr.*, 1882, 375—379).—The parotid gland yields saliva to the amount of about 1000 grams per hour; this fluid is at first thick, then becomes clear and thin, of alkaline reaction, and having a sp. gr. 1·006—1·0075. Exposed to the air, it becomes opaque owing to the formation of calcium carbonate; it contains albuminoids, fat, chlorine, phosphates, sulphates, potassium, sodium, lime, and magnesium, but no thiocyanates. The saliva secreted by the sub-maxillary gland is at first clear and colourless, becoming thick and ropy; it is not so readily affected by exposure to the air, and from it alcohol precipitates mucin and ptyalin; starch is converted into sugar by it, and it does not contain thiocyanates. The mixed salivas, which were collected by means of a T canula inserted into the gullet, are colourless and clear, but soon change into an opalescent liquid, are alkaline,

and have a sp. gr. 1·0004; they contain considerable quantities of chlorides, and but small amounts of the other inorganic salts. Their action on starch is energetic. Fat, ptyalin, and mucin are present, but no thiocyanates.

*Analyses of Saliva (average per 1000 parts).*

	Parotid.			Submaxillary.	Mixed. Sp. gr. 1·0075–1·007.
	Sp. gr. 1·006–1·0075.	Sp. gr. 1·005.		Sp. gr. 1·0035–1·003.	
		Clear.	Thick.		
Water .....	991·613	993·118	991·689	992·500	989·152
Dry matter .....	8·387	6·882	8·311	7·500	10·846
Salts .....	5·958	4·274	3·404	2·575	8·197
Organic matter ....	2·429	2·608	4·817	4·925	2·649

*Quantitative Analyses of Organic Matter (in 1000 parts).*

Acid albuminate....	0·087	—	—	0·580	0·680
Albumin .....	1·740	—	—	—	1·000
Fat .....	0·017	—	—	—	0·50
Mucin .....	—	—	—	3·580	3·800

The saliva possesses powerful diastatic properties, converting starch in half an hour into achroödextrin and sugar; after 15 seconds the erythrodextrin is to be found, and sugar after a quarter of an hour; in the animal, this conversion takes place in the mouth, when oats, hay, straw, are given, but potato-starch is converted in the stomach. In the parotid, a saliva peptonising ferment is found in small quantity, which only acts on fibrin and not on albumin. The mixed salivas contain also a peptonising ferment. Cellulose is not dissolved by the saliva.

E. W. P.

**Richness in Oxygen of the Blood of Animals Living in Elevated Regions.** By P. BERT (*Compt. rend.*, 94, 805–807).—The blood of different herbivorous animals acclimatised at an elevation of 3700 meters was found by the author to be much richer in oxygen than the blood of similar animals inhabiting lands near the sea-level. 100 c.c. of the blood contained from 16·2 to 21·6 c.c. of oxygen in the cases of animals from the elevated region, whereas the amount for animals in France is only 10 to 12 c.c.

R. R.

**Occurrence of Acetoacetic Acid in Urine.** By R. v. JAKSCH (*Ber.*, 15, 1496).—The author has isolated from urine a body having the reactions and properties of acetoacetic acid, and has the subject under further investigation.

C. F. C.

**Researches on the Cause of Tuberculosis.** By KOCH, BAUMGARTEN, and TOUSSAINT (*Bied. Centr.*, 1882, 387–390).—Bacillæ in the

blood appear to be the cause of this disease, and they may be detected in the serum by a mixture of alkaline methylene-blue, and vesuvine, whereby they alone are coloured blue. Cultivated bacillæ when introduced into the animal, produce all the ordinary symptoms of tuberculosis, and it is thought that they alone are the cause of illness. They do not lose their power of infecting even after drying for eight weeks: hence it is possible that excreta from diseased persons may be the means of transmitting the disease to healthy individuals.

E. W. P.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Schizomycetic Fermentation.** By A. FITZ. Part VII. (*Ber.*, 15, 867—880).—To obtain a crop of *Bacillus butylicus* unmixed with other spores, a liquid containing this ferment is diluted with water until a drop of the mixture does not contain more than a single germ. One drop of the liquid is then brought into a flask containing a 3 per cent. solution of sugar, mannitol, or glycerol, 1 per cent. of meat extract, and pure calcium carbonate, this mixture having been previously sterilised by exposure to a temperature of 110°.

A temperature of 40° is most favourable for the growth of the *bacillus*; between 45° and 45·5° it ceases to produce fermentation. The spores are destroyed by exposure to a temperature of 100° for 5 to 15 minutes, or by a more lengthened exposure (6 to 11 hours) at a lower temperature, which must not, however, be below 80°. Fermentation is stopped by the addition of 2·7—3·3 per cent. of ethyl alcohol, or of 0·9 to 1·05 per cent. of butyl alcohol, or 0·1 per cent. of butyric acid. The bacillus continues to grow in a liquid containing 25 per cent. of glycerol. It also thrives in solutions of calcium lactate, glycerate, malate, tartrate and citrate, ammonium lactate and tartrate, erythrol, milk-sugar, and quercite, although it does not induce fermentation in these liquids.

100 parts of glycerol, mannitol, or invert sugar, yield the following products when decomposed by the *Bacillus butylicus* :—

	Glycerol.	Mannitol.	Invert sugar.
Butyl alcohol .....	8·1	10·2	0·5
Butyric acid .....	17·4	35·4	42·5
Lactic „ .....	1·7	0·4	0·3
Succinic „ .....	—	0·01	trace
Trimethylene alcohol ....	3·4	—	—

*Bacillus butylicus* which has been cultivated in an unfermentable liquid freely exposed to the air, loses its power of acting as a ferment. The *enzym* inverts a solution of cane-sugar, but has no action on milk-sugar, urine, or starch. It slowly dissolves insoluble albumin.

W. C. W.

**Action of Hydrogen Dioxide on Ferments, &c.** By P. BERT and P. REGNARD (*Compt. rend.*, 94, 1383—1386).—It has been stated by Dumas, in his report on Béchamp's works, that blood fibrin is the only animal matter which decomposes hydrogen dioxide. The authors find, however, that all fermentation produced by an organised ferment is arrested by hydrogen dioxide, and the ferment is killed; but soluble ferments as saliva, diastase, &c., are not acted on by it.

Hydrogen dioxide is not acted on by fats, starch, egg-albumin, casein, fibrin, creatine, creatinine, or urea, but it is rapidly destroyed by musclin, blood fibrin, and different nitrogenous vegetable substances. This action ceases at a temperature of 70°.

L. T. O'S.

**Ropy Milk.** By A. SCHMIDT (*Landw. Versuchs.-Stat.*, 28, 91—109).—The ropy condition which milk sometimes assumes is due to the presence of a micrococcus which has a diameter of 0.001 mm. This ferment acts on the saccharine matter, and not on the casein, with production of mucilage. This mucilage can be precipitated by alcohol from a ropy solution of lactose. During this mucic fermentation, no production of mannitol or carbonic anhydride was noticed, and this observation is therefore opposed to those of Pasteur. Sound milk, contaminated to the amount of  $\frac{1}{20000}$  with this ropy milk, assumes a like condition, as does also whey. Solutions of 1—5 per cent. lactose are affected most at temperatures of 30—40°; 60° is fatal to the fermentation, although the ferment is not destroyed at 100°. It is necessary for fermentation that phosphates, sulphates of potassium, and magnesium be present, as is also the presence of a trace of albuminoids, preferably in the form of peptones; neither nitrates nor salts of ammonium support the life of the ferment. The addition of 0.5—1 per cent. boric acid preserves the milk from fermentation for a week, and 5 per cent. of this substance completely kills the ferment.

E. W. P.

**Separation of Free Nitrogen during Putrefaction.** By B. E. DIETZELL (*Bied. Centr.*, 1882, 417—420).—Animal matter, when putrefying, evolves a certain amount of nitrogen in the free state. This is due to the action of free nitrous acid on the amides present. To obviate this loss, an excess of calcium carbonate must be added to the decomposing mass.

E. W. P.

**Structure of Starch Grains.** By A. MEYER (*Bied. Centr.*, 1882, 396—398).—Meyer believes with Schimper that the growth of starch grains occurs according to the apposition theory. He, however, does not agree with Schimper's explanation, and brings forward reasons to show that the growth must be explained after a different manner.

E. W. P.

**Woody Substance and Lignified Tissues.** By M. SINGER (*Monatsch. Chem.*, 3, 395—411).—Woody tissues are commonly supposed to contain, together with cellulose, a body richer in carbon, called *Lignin* or *Woody substance*, which determines their physical and chemical characters, and masks the reactions of cellulose with iodine



solution and sulphuric acid, with zinc chloride, and with cuprammonia. The lignification of tissues has indeed hitherto been inferred, not so much from any definite reaction of lignin, as from the absence of the usual cellulose reactions, and from the physical characters of the tissues. Runge and Hofmann, on the other hand, had observed that a deal shaving is coloured yellow by colourless salts of aniline, toluidine, naphthylamine, leucoline, sinnamine, &c.; and it was afterwards observed by other chemists that the same colour-reaction is produced with various woods, both hard and soft; but Wiesner was the first to show that this reaction is characteristic of lignification, not only in wood properly so called, but likewise in all other lignified tissues, as elder-pith or the indurated tissues of mangold-wurzel. He further suggested for this purpose the use of *aniline sulphate*, which is now universally employed in microchemical investigations.

A much more delicate test proposed by v. Höhnelt is the so-called *Xylophylin*, obtained from cherry-wood extract, which was shown by Wiesner to consist of *phloroglucol*, or a mixture of that compound with catechol; in contact with woody tissue, it produces, on addition of hydrochloric acid, a deep red-violet coloration. A similar but fainter colour is produced by *catechol* and *resorcinol*, in both cases with addition of hydrochloric acid. *Pyrogallol* with hydrochloric acid produces a faint dove-grey colour. *Orcinol* reacts like phloroglucol. A mixture of phenol and hydrochloric acid, added to lignified tissues in direct sunshine, produces, especially after the drying of the preparation, a blue-green to sky-blue colour. The delicacy of this reaction is greatly increased by addition of potassium chlorate. Hydrochloric acid alone colours lignified tissues more or less yellow; but the coloration thus produced is very faint and transient. An extremely delicate test is *pyrroline*, which, in union with hydrochloric acid, imparts to lignified membranes a deep cherry-red colour, which, however, very quickly decomposes, and is permanent only in very dilute solutions. Lastly, unmistakable reactions for lignified tissue are afforded by *indole*, and by *resorcinol* in combination with sulphuric acid, indole producing a bright rose-red, resorcinol a violet or deep-red colour, accordingly as the acid is added in small quantity or in excess.

Of all these reagents, the author gives the preference to phloroglucol mixed with hydrochloric acid. Indole is indeed the most delicate; but an objection to it—in addition to its high price—is, that it must be used in conjunction with strong sulphuric acid, which destroys all vegetable tissues, and therefore requires to be employed with great caution. Pyrroline is also very delicate, but it is difficult to obtain, and very unstable.

*Nature of "Lignin."*—By means of the above-described reagents, the author has endeavoured to decide the question as to whether the substance usually called lignin, and described as insoluble in water, alcohol, non-oxidising acids, and moderately dilute alkaline liquids, is a distinct chemical individual, or a mixture of several compounds. His results are as follows:—

When wood, or lignified tissue in general, is subjected to the action of boiling water, several bodies may be extracted from it, and sepa-

rated one from another by a variously prolonged application of the process. These bodies are:—

1. A substance characterised by the above-mentioned reactions (with aniline sulphate, phloroglucol, indole, pyrroline, &c., mixed with the corresponding acids); also by an odour of vanilla emitted by the concentrated extract, and not removable from the tissue by the action of boiling water continued even for 10 hours daily for six weeks, to such an extent as to lead to any considerable diminution in the distinctness of the reactions, either in the extract or in the residual wood. Now experiment shows that pure vanillin, treated with the same reagents, exhibits the colours shown to be characteristic of lignification, and that, like the substance contained in lignified tissues, it is easily dissolved by hot water, soda-ley, and alcohol, and is decomposed by heat at the same temperature as the latter. The body in question is, therefore, vanillin, which thus appears to be very widely diffused in the vegetable kingdom.

2. A body, coloured more or less sky-blue by a mixture of potassium chlorate, phenol, and hydrochloric acid, but no longer recognisable after about 18 days' boiling, either in the extract or in the residual wood. The reactions show that this body is coniferin.

3. A kind of gum precipitated from the aqueous extract by alcohol; amorphous, easily soluble in water and frothing. It is distinguished from T. Thomsen's wood-gum (1879, Abstr., 613) by its appearance, its greater solubility in water, and its abundant occurrence in pine-wood. Thomsen's wood-gum is, according to Singer's experiments, not confined to wood, but is a constant constituent of lignified tissues.

4. A substance coloured yellow by hydrochloric acid, and extractable by water in a few days; its chemical nature has not yet been determined.

The exact relation of these bodies to the hypothetical lignin cannot be decided by the experiments above indicated; but the manner in which they can be extracted one after the other from wood by water renders it probable that the so-called lignin is a mixture of several chemical individuals.

H. W.

**Analysis of the Leaves of Memecylon Tinctorum.** By DRAGENDORFF (*Chem. Centr.*, 1882, 382).—100 parts of the air-dried leaves contain:—

	Pts.
Moisture.....	12·65
Sand .....	2·31
Ash containing 0·72 per cent. $P_2O_5$ .....	10·48
Fatty oil soluble in light petroleum.....	0·66
Ethereal oil .....	traces
Waxy substance.....	0·66
Resin soluble in ether and alcohol .....	1·35
Resin insoluble     "     " .....	3·24
Glucosides soluble in alcohol .....	1·47
Glucose insoluble     "     " .....	2·35
Mucilage soluble in water .....	3·70
Albumin precipitable from aqueous solutions .....	traces

	Pts.
Albumin not precipitable from aqueous solutions....	1·56
Albuminous substances, &c., soluble in dilute soda-ley	0·94
Albuminous substances insoluble in dilute soda-ley..	16·03
Cellulose.....	15·03
Substances resisting chlorine .....	7·20
Wood gum .....	6·00
Substance resembling pararabin.....	3·83
Metarabic acid .....	4·02
Substance resembling tannic acid .....	2·54
Tartaric and malic acids .....	1·38
Oxalic acid in the calcium oxalate .....	1·44
Substances from aqueous extract not examined ....	5·87
Lignin and cuticular substances .....	5·09

D. B.

**Analysis of Kola Nuts.** By E. HECKEL and F. SCHLAGDEN-HAUFFEN (*Compt. rend.*, 94, 802—805).—The kola nut, which is the produce of *Sterculia acuminata*, a plant growing in equatorial Africa, has been analysed by the authors with following results:—*Substances soluble in chloroform.*—Caffeine, 2·348; theobromine, 0·023; tannin, 0·027; fatty matters, 0·585. *Substances soluble in alcohol.*—Tannin, 1·591; Kola red, 1·290; glucose, 2·875; fixed salts, 0·070. *Other substances.*—Starch, 33·754; gum, 3·040; colouring matters, 2·561; proteids, 6·761; ash, 3·525; water, 11·919; cellulose, 29·831. Total, 100·000.

R. R.

**Occurrence of Hypoxanthine in Potatoes.** By E. SCHULZE (*Landw. Versuchs.-Stat.*, 28, 111—115).—The presence of hypoxanthine (this volume, p. 885) in the juice of potatoes has been ascertained, and it has been prepared by dialysis of the juice after removal of the albuminoids. A crystalline compound is formed by the addition of ammoniacal silver nitrate to the dialysed liquid. One c.c. of the juice contained about 0·0037 gr. of hypoxanthine.

E. W. P.

**Black Hellebore Root.** By A. HERLANDT (*Pharm. J. Trans.* [3], 13, 62).—As the microscopic examination of the rhizomes of *Helleborus niger* reveals no characteristic peculiarities, chemical reactions must be utilised for its recognition. If to a filtered decoction of the rhizomes one-third of hydrochloric acid be added and the mixture boiled, the clear liquid becomes turbid and assumes a peculiar violet colour. After cooling, black flocks separate, which, when washed with ether, are of a deep violet colour. In the case of the rhizome of *H. viridis*, the colour after the action of the acid is at first more green. The rhizomes of *Actaea* and *Polygala senega* give, when treated in the same manner, no similar reaction. This reaction is due to helleboretine, which is not present in the rootlets, and is adapted for the detection of helleboretine in poisoning cases, if only allowance be made for slight change of colour due to foreign colouring matters in the fluids under examination.

E. W. P.

**Importance of Starch in Belladonna Roots.** By F. BUDDER (*Arch. Pharm.* [3], 20, 414—416).—It frequently occurs that starch is absent from the roots, or parts of the roots of the belladonna; examination of the amount of atropine present shows that the alkaloid is always present in larger quantities when starch is also present. It is the young plant which appears to contain little or no starch, and the percentage of alkaloid increases as the plant ages.

E. W. P.

**Active Principle of Adonis Vernalis.** By V. CERVELLO (*Pharm. J. Trans.* [3], 13, 129).—This plant contains a non-nitrogenous, colourless, odourless, bitter substance, which the author terms *adonidine*; this, although very energetic, is present in but small quantities in the plant, from which it may be separated by maceration with 50 per cent. alcohol. After removal of the nitrogenous matter by lead, the base is combined with tannic acid, and the resulting compound decomposed by zinc oxide. As compared with digitalin, the physiological action of adonidine is very similar, but it is not cumulative, and is far more powerful.

E. W. P.

**Presence of a Second Poisonous Principle in Thevetia Nereifolia.** By C. J. A. WARDEN (*Pharm. J. Trans.* [3], 13, 42).—In the kernels of the above-mentioned plant there exists another poisonous principle, besides thevetine already discovered and described. This second principle was obtained by precipitating the mother-liquor left after the crystallisation of thevetin, by aqueous tannic acid, and decomposing the precipitate by lime. The yellow extractive obtained by alcohol is bitter, non-crystalline, and soluble in water. Concentrated nitric or sulphuric acid produces a yellow coloration, hydrochloric acid has no effect; potassium dichromate and other oxidisers likewise produce no change, whereas it is precipitated white by tannic acid.

E. W. P.

**St. Petersburg Rhubarb.** By PRZEWALSKI (*Arch. Pharm.* [3], 20, 451).—Chinese rhubarb grown near St. Petersburg was examined. The dried roots of these varieties were extracted with benzene, and the residue, after evaporation of the benzene, boiled with soda solution. The emodine is found in the solution when cold, and the chrysophanic acid in the residue. In this way  $\frac{1}{4}$  per cent. trace of emodine was found, and  $\frac{3}{4}$ — $\frac{1}{2}$  per cent. chrysophanic acid. As the yield of chrysophanic acid and emodine is good, it is to be regretted that *Rheum palmatum* is no longer cultivated in Russia, which draws its supplies from England.

E. W. P.

**St. Petersburg Rhubarb.** By F. BEILSTEIN (*Ber.*, 15, 901—902).—An examination of the roots of *Rheum palmatum* and *Rheum officinale* grown in St. Petersburg, shows that the largest quantity of active constituents is contained in the former variety. 0.5 per cent. of chrysophanic acid was obtained from the roots of *Rheum officinale*. *Rheum palmatum*, grown in clayey soil, contained 0.5 per cent. chrysophanic acid and a trace of emodine; but the same plant cultivated

in sandy marshy ground, contained more than 0.75 per cent. of chrysophanic acid, and more than 0.25 per cent. emodine.

W. C. W.

**Influence of the Weight of the Seeds on the Yield of the Crop.** By BIRNER and TROSCHE (*Bied. Centr.*, 1882, 320).—The seeds of oat and bean plants sown were divided into heavy, medium, and light, with the result that the best crops were obtained from the heaviest seed.

E. W. P.

**Composition of Italian Fodders.** By A. FUNARO (*Landw. Versuchs.-Stat.*, 28, 119—122).—This paper consists of the analyses of hay, lucerne, maize, and mulberry leaves, as grown in Italy.

E. W. P.

**Composition of Hay Grown under the Influence of different Manures.** By J. KÖNIG (*Bied. Centr.*, 1882, 428).

Calculated in dry, free from sand.	Unmanured.	Bone-meal.	Tribasic calcium phosphate.	Bibasic calcium phosphate.	Retrograde phosphate.	Soluble phosphate.
<i>1st Cut.</i>						
Albuminoids.....	8.09	8.37	7.98	9.33	8.50	8.78
Fat.....	3.65	3.34	3.52	3.55	3.95	4.04
Extractive.....	49.04	47.92	48.28	47.48	48.28	47.15
Fibre.....	32.63	33.75	33.68	32.73	32.04	32.81
Ash.....	6.59	6.62	6.54	6.91	7.23	7.22
Per cent. $P_2O_5$ in ash...	0.307	0.326	0.396	0.486	0.588	0.778
"    "    "    ...	4.66	4.93	6.06	7.01	8.14	10.77
<i>2nd Cut.</i>						
Albumin.....	10.56	11.13	10.81	10.86	11.19	—
Fat.....	5.16	6.30	5.65	5.18	5.05	—
Extractive.....	48.13	46.02	45.22	45.9	45.48	—
Fibre.....	27.7	27.86	29.44	28.76	29.35	—
Ash.....	8.45	8.65	8.88	9.30	8.93	—
Per cent. $P_2O_5$ in ash...	0.468	0.513	0.550	0.631	0.705	—
"    "    "    ...	5.53	5.93	6.19	6.79	7.90	—

E. W. P.

**Composition of "Timothy Grass" at different Periods of Growth.** By W. H. JORDAN (*Bied. Centr.*, 1882, 393).—Two plots of this grass were selected, the one manured and the other unmanured, and crops were cut at three periods of growth. As growth proceeds, a reduction of fat, nitrogen, and ash occurs, while fibre and extractive increase. Also a relative reduction of the amido-nitrogen, as compared with the albuminoid nitrogen, takes place. Manuring with bone-meal, potassium chloride, and ammonium sulphate, raises the percentage of nitrogen, especially that in the form of amides, as well as the ash and fibre; so that the quality as well as quantity of the crop is raised by the use of manures.

E. W. P.

**Diastatic Action of Certain Fodders.** By F. SESTINI and R. FUNARO (*Landw. Versuchs.-Stat.*, 28, 118).—The diastatic action of some fodders is generally ascribed to an excess of albuminoids, but the truth of this theory is not certain. Lucerne, vetches, and hay, were treated with alcohol; the first yielded 14.8 grams, the second 10.9 grams, the last 6.2 grams of extract, and of this extract, the following percentages consisted of resinous matters, 2.1, 0.9, 0.25. The authors consider that these small quantities of resin would not have much effect, but that the effects observed must be due to other matters present in the extract, for that of the lucerne was bitter and unpleasant, resembling quassia or senna. E. W. P.

**Preparation and Preservation of Various Fodders.** By J. KÖNIG (*Bied. Centr.*, 1182, 379—384).—König recommends that green maize be pitted and allowed to ferment, after which it may be given with flesh-meal or oil-cake. By fermentation, it loses some of its carbohydrates, whereby the ratio of fibre to extractive is reduced to 1 : 1 instead of 1 : 2.5, as in the fresh grain; but on the other hand, "sour maize" contains lactic acid and aromatic compounds, which render it more acceptable to cattle and more easily digestible. F. Anthon mixes at 60° 100 parts dried brewers' grains with 8.3 parts beetroot molasses; to this he adds 33.3 parts barley or wheat bran, and then bakes the dough produced.

Müntz finds that grain yields carbonic anhydride when exposed to the air, in double the quantity that is evolved when the grain is kept in closed vessels. The volume of oxygen absorbed by grain is greater than that of the carbonic anhydride set free, consequently a secondary and incomplete oxidation, similar to that occurring during the germination of oleaginous seeds, must be taking place. As the moisture increases in the seed so does the production of carbonic anhydride increase, for dry grain yields but little of this gas; also a rise of temperature up to 50° increases the yield, but at 50° it ceases; above that temperature there is, however, a much greater evolution of gas. The practical conclusions drawn are that in granaries the grain must be kept dry, of an equable temperature, and excluded from air as far as possible. E. W. P.

**Physical Properties of the Soil in a Close or Open Condition.** By E. WOLLNY (*Bied. Centr.*, 1882, 363—365).—*Amount of Water in the Soil.*—The theory that the more open the soil is the quicker it dries, has been disproved by several authors, who have shown that a close soil dries the more rapidly, whence they conclude that rolling assisted evaporation. This conclusion is unwarranted, as the amount of water in a soil is not dependent on the evaporation from the surface only, but also on the permeability, &c. The author has investigated various soils to ascertain the circumstances affecting the quantity of water present. (1.) More water evaporates from a soil when it is close than when it is open, because, by the compression of the particles together, the movement of the water from below upwards is accelerated, and therefore the loss occurring from the surface is more easily replaced. For this latter reason, the closer the particles are the longer the surface remains moist. (2.) Close

soils possess a greater capacity for water, because of the reduction in the number of the non-capillary passages, and conversion of the same into capillaries, hence the downward passage of water is retarded. (3.) The action referred to in (1) occurs only when, after the change from the open to the close state, continued dryness sets in; as a rule the properties mentioned in (2) are those which are the most effective. (4.) It is advisable in general to bring the soil to a certain extent into a compact condition, whereby the amount of water present is raised.

*The Temperature of a Soil Open and Compact.*—Heat passes downwards with greater ease the closer the particles are together, for then the amount of the bad conductor air is reduced, and water, a good conductor, is increased in quantity. In warm weather, the temperature of the soil is higher the more compact the soil, and the same reasoning holds good for the variation of temperature.

*Formation of Clefts, &c.*—Clefts formed by drying are most numerous in soils of unequal texture, and are of greater breadth and depth in open soil. This arises from unequal distribution of water, and the greater or lesser coherence of soil of different degrees of compactness. E. W. P.

**Changes Effected by Cultivation of Forest Lands.** By HANAMANN (*Bied. Centr.*, 1882, 366).—Forest land was broken up, and various crops were grown on it during four seasons. The soil was periodically examined for matters soluble in hydrochloric and acetic acids. The lime, compared with the other constituents, appeared to be in a very soluble condition, but only one-tenth of the phosphoric acid was in an easily soluble condition (*i.e.*, soluble in acetic acid), and this proportion was not appreciably altered by cultivation and by the manuring in the fourth year; but most likely in future years the amount of acid would be considerably reduced. A reduction in the potash is not to be feared, as the soil is rich in this constituent. E. W. P.

**Experiments on the Manuring of Vines.** By P. WAGNER and C. STÜNKEL (*Landw. Versuchs.-Stat.*, 28, 123—149).—These experiments are a continuation of those described previously (*ibid.*, 25, 247), and were instituted for the purpose of deciding the effect on the quality and quantity of the must produced by vines when manured with phosphoric acid, potash, and nitrogen. The plots were in quadruplicate, and were five in number, one plot being devoted to unmanured vines, whilst to the others were added 100 kilos. soluble phosphoric acid, 100 kilos. soluble phosphoric acid, and 80 kilos. potash, 100 kilos. soluble phosphoric acid, 80 kilos. potash, and 30 kilos. nitrogen; the potash being in the form of chloride, and the nitrogen as ammonium sulphate. It was also arranged that these experiments should be conducted simultaneously on six different vineyards in Rhein-Hesse. A series of tables of the results obtained is given, and these have reference to the percentage of sugar and acid in the must, as well as the total yield of must. From these we gather that potash and nitrogen manures do not produce an increase of yield which pays for the extra expense; in some cases, soluble phosphates have produced an increase, but in others its action was detrimental. The

percentage of sugar and acid is not raised by phosphates. The employment of artificial manures instead of stable dung may produce better results, but on the whole, although the total yield of must is raised, there is no very great gain.

E. W. P.

**Use of Superphosphates on the Calcareous Soils of the South-East of France.** By DE GASPARIN (*Compt. rend.*, 94, 766—768).—The author finds that one-sixth of the phosphoric acid contained in the natural phosphates used as manures in the south-east of France is insoluble in water. Superphosphate, on the contrary, increases the crop to such an extent as to amply repay for the cost of the manure.

R. R.

**Manuring Experiments at Königsberg.** By KLIEN (*Bied. Centr.*, 1882, 373—375).—These were a continuation of experiments commenced in 1880, and show the after-action of various phosphates in the following years. Generally it was found that phosphates in combination with nitrogen continue to produce their effects in the two succeeding years after their introduction into the soil. Phosphates alone are also of value, but precipitated is better than dissolved. Analysis of the soil shows that those which contain much phosphoric acid in their finest portions produce the lowest yield on the addition of pure phosphates.

E. W. P.

**Manuring Experiments on Potatoes and Barley.** By L. KOCH (*Bied. Centr.*, 1882, 372).—Potatoes and barley were manured with varying quantities of guano superphosphate (7 per cent. N, and 10·5 per cent. soluble phosphate) on six stations. In nearly all cases there was a gain over the unmanured plots, when the value of the manure was considered. Guano reduced the starch in the tubers; barley was affected only by strong applications.

E. W. P.

**Potash Salts as Manures for Sugar-beets.** By M. MÄRCKER (*Bied. Centr.*, 1882, 369—372).—The addition of kainite or gypsum to the manures ordinarily employed in the cultivation of sugar-beet raises the percentage of sugar and the quotient of purity alike, but the kainite likewise considerably increases the total yield of roots. In wet seasons the application of potassium chloride is useless, but a gain is obtained by its use in dry weather.

E. W. P.

**Carnallite as a Manure and Fixer of Ammonia.** By J. FITTBOGEN (*Bied. Centr.*, 1882, 368).—The values of carnallite, gypsum, kainite, and waste salts as fixers of ammonia were compared. Carnallite appears to be the best fixant, although the others act well; the former fixes 81·7 per cent. of the total ammoniacal compounds, and the quantities required for the dung of ten sheep are 0·25 kilo. gypsum, 0·3 kilo. carnallite, and 0·2 kilo. kainite per day, but these quantities may be reduced in cold weather.

E. W. P.

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## Analytical Chemistry.

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**Some Points in the Construction of an Apparatus for the Accurate Analysis of Gases.** By E. W. MORLEY (*Chem. News*, 45, 273).—1. When a certain method of determining the top of the pressure column is used, the conditions of most accurate measurements of varying volumes of gas are satisfied by making the column of mercury, which measures the pressure, equal in length to the part of the eudiometer which is filled with gas.

2. To define the top of the pressure column, a Jolly-point enclosed in the barometric vacuum is used, which makes the probable error at the top of this column evanescent. The whole error of the tension is therefore produced by the same uncertainty which produces the error in the observed volume.

3. To preserve the barometric vacuum over the pressure column, this column is shut off from communication with the rest of the apparatus, except at the instant of a measurement.

4. An auxiliary pressure-tube is employed for preliminary adjustment.

5. The eudiometer tube is graduated in half millimeters by fine lines not over the eight-thousandth of an inch wide. The graduation is affected with no relative errors of the hundredth of a millimeter. A reading microscope is carried on a cylinder so solidly connected with the iron tripod of the apparatus, that ten pounds produce a relative flexure of only a tenth of a millimeter. This microscope is brought nearly to the level of the mercury in the eudiometer, when the column in the pressure-tube reaches just to the Jolly-point. The microscope is made to give distinct vision of the graduation, and by Grunow's cathetometer fine adjustment, the terminal lines of the eye-piece micrometer are made to coincide with two millimeters of the graduation. The focussing movement now moves the microscope, so that distinct vision is had of the meniscus, and the level of the mercury is read to the hundredth of a millimeter on the eye-piece micrometer, whose divisions now represent the divisions of the tube carried forward into its interior. A four-inch objective, with an amplification of about sixty diameters, is used.

6. The sum total of all the errors of this reading is equivalent to no more than a probable error of one-hundredth of a millimeter in this determination; and in the calibration of the apparatus, made before much practice in the use of this reading arrangement, the probable error of a reading was the hundredth of a millimeter.

7. The probable error of a single determination of oxygen in air is less than the four-hundredth of a per cent.

8. The method of measurement is adapted to rapid computation. The whole reduction of three measurements in an analysis, so as to obtain the percentage of oxygen, takes less than two and a half minutes.

D. B.

**Solubility of Gases in Absorption Liquids.** By W. HEMPEL (*Ber.*, 15, 910—911).—In gas analysis, the error due to the slight solubility of the gases in the liquids used as absorbents, may be avoided by making two analyses of the mixed gases in rapid succession. The second analysis yields correct results. W. C. W.

**Solubility of Gases in Vulcanised Caoutchouc.** By W. HEMPEL (*Ber.*, 15, 912—913).—A piece of caoutchouc tubing 3 cm. in length and 4—5 mm. in diameter can absorb 0.2 c.c. of carbonic anhydride and 0.9 c.c. of nitrous oxide. This fact shows the necessity of avoiding the use of caoutchouc in the construction of apparatus used for gas analysis. W. C. W.

**Action of Lead and Manganese Dioxides on the Haloid Salts of the Metals in presence of Acetic Acid.** By C. L. MÜLLER and G. KIRCHER (*Ber.*, 15, 812—813).—Voitmann (*Ber.*, 13, 325) has proposed to separate chlorides from bromides and iodides by the action of lead dioxide and acetic acid, which decomposes the last two mentioned classes of salts only; and to separate iodides from bromides by means of manganese dioxide and acetic acid, which decomposes the former only. The authors, however, find that chlorides are decomposed by lead dioxide and acetic acid, with liberation of chlorine and formation of monochloroacetic acid, which is partially oxidised to carbonic anhydride, lead chloride being formed at the same time. When manganese dioxide is used, no chlorine is liberated, but carbonic anhydride and manganese chloride are formed. Lead dioxide and acetic acid are without action on bromides and iodides, but manganese dioxide and acetic acid react alike on bromides and iodides. With regard to the action of these peroxides upon neutral solutions of the haloid salts of the alkali-metals, the authors find that the chlorides are not decomposed, and that the bromides and iodides are but slowly acted on. P. P. B.

**Estimation of Nitrous Oxide.** By W. HEMPEL (*Ber.*, 15, 903—910).—Bunsen's mode of estimating nitrous oxide by exploding with hydrogen, yields more exact results than any other method yet proposed. The hydrogen and nitrous oxide should be present in the ratio of 2 or 3 to 1. When the nitrous oxide is mixed with air or nitrogen, from 26 to 64 volumes of "detonating gas" should be added for every 100 volumes of non-combustible gas present. The author was not able to prepare perfectly pure nitrous oxide. The purest specimen contained 98.8 per cent. of nitrous oxide. W. C. W.

**Quantitative Estimation of Potassium and Sodium.** By W. KNOP (*Chem. Centr.*, 1882, 347).—For some time, the author has used hydrofluoric acid for the analysis of silicates, and he now proposes to use this acid for the determination of alkalis in non-siliceous substances. The required quantity of silicon fluoride is produced by adding hydrofluoric acid and pure silicic acid to the substances, in order to convert the potassium or sodium contained therein into metallic silicofluoride. The alkalis are then extracted by means of a

mixture of alcohol and ether, acidified with hydrochloric acid. Potassium and sodium silicofluorides are insoluble in this mixture, but the chlorides of the metals, from which these alkalis have most frequently to be separated, dissolve with ease in the same and are removed by decantation. The advantage which this method has over that usually employed for determining potassium and sodium consists in the circumstances that these alkalis are at once concentrated in the form of a precipitate of small volume and weight, which may be collected on a small filter, and requires only a small quantity of water to wash it. The chief advantage, however, is that the solutions of the alkalis, which in order to recover the latter are finally evaporated as sulphates, can be prepared in a concentrated state. As an example of the mode of procedure, the author gives a description of the analysis of a mixture of the chlorides of potassium, sodium, iron, calcium, and magnesium. The results obtained are very satisfactory.

This method of determining potassium and sodium is of special advantage in cases where it is not intended to separate these alkalis directly, but where the result is calculated from the quantity of sulphates found, and the quantity of sulphuric acid contained therein as determined by barium chloride. The author has calculated the constant factors obtained by using Richter's equations, employing the atomic weights as recently corrected by Stas :—

By taking—

$$\begin{array}{rclclcl} \text{Na} & = & 22.98, & \text{K} & = & 39.04, & \text{Ba} & = & 136.80, & \text{O} & = & 15.96 \\ \text{Na}_2\text{O} & = & 61.92, & \text{K}_2\text{O} & = & 94.04, & \text{BaSO}_4 & = & 232.62, & \text{SO}_3 & = & 79.86 \end{array}$$

and calling P the weight of sulphate obtained,  $x$  the quantity of potassium oxide contained therein,  $y$  the quantity of sodium oxide sought, and S the quantity of sulphur trioxide determined by barium chloride and combined with  $x + y$ , so that therefore

$$1. \quad P = x + y + S,$$

we obtain by making use of Richter's equations :—

$$2. \quad y = S \times 4.19782 - P \times 1.92777.$$

In both equations S and P are quantities which can never be equal to 0 whilst  $y = 0$  when the quantity of sulphate contains no sodium, and consists therefore of pure potassium sulphate and *vice versa*  $x = 0$  when pure sodium sulphate is present.

The preceding equation (2) can therefore be proved with great ease as to the utility of the two constant factors contained therein, by giving  $P = 86.95$ , half the atomic weight of potassium sulphate,  $S = 39.93$ , half the atomic weight of sulphur trioxide. In order to solve the second equation,  $y$  must equal 0, or  $S \times 4.19782$  must equal  $P \times 1.92777$ . By calculating  $y$  in this manner with the use of the equation—

$$y = 39.93, 4.19782 - 86.95, 1.92777,$$

we obtain for both products agreeing with one another to the second decimal place—

$$y = 167.62 - 167.62, \text{ i.e. } = 0.$$

This test is of great importance, inasmuch as it confirms the accuracy of the atomic weights corrected by Stas. D. B.

**Silver Plumbite and Quantitative Estimation of Silver in Lead Ores.** By J. KRUTWIG (*Ber.*, **15**, 1264—1267).—The author in a previous communication (this vol., p. 774) has described the quantitative determination of the golden precipitate thrown down by sodium hydroxide in mixed solutions of lead and silver salts; in the present paper the composition of this precipitate is more minutely examined, as the author's results do not agree with those of Wöhler (*Pogg.*, **41**). Analysis showed that the precipitate has the composition  $\text{AgPbO}_2 \cdot 2\text{H}_2\text{O}$ , which can be regarded as the silver salt of a plumbous acid, formed by the action of silver nitrate on potassium plumbite (or solution of lead hydroxide in potash), thus:  $\text{Pb(OK)}_2 + 2\text{AgNO}_3 = \text{Pb(OAg)}_2 + 2\text{KNO}_3$ . The lead and potassium salts are thus analogous to the well known lead plumbate.

Spring endeavoured to obtain this golden compound by subjecting a mixture of equal molecules of lead hydroxide and silver oxide to a pressure of 7500 atmospheres, but the experiment was unsuccessful, the resulting block manifesting no signs of decomposition.

The author made a further series of experiments on the accuracy of the determination of silver in lead ores by the wet way by means of the silver plumbite; this is dissolved in nitric acid, and the silver precipitated as chloride, which is either weighed as such or dissolved in ammonia, and the metallic silver thrown down by electrolysis. This method is found to be very accurate, provided that the proportion of silver to lead is not less than 1 : 1500, so for lead ores, poor in silver, a large quantity of the ore must be dissolved to ensure accuracy. V. H. V.

**Analysis of Iron and Steel, with special reference to the Estimation of Carbon and Silicon.** By F. WATTS (*Chem. News*, **45**, 279).—The author mentions that in none of the processes commonly adopted for the estimation of silicon in iron and steel, is any distinction observed between the silica resulting from the oxidation of the silicon, and that which exists ready formed in combination with various bases in the form of mechanically intermingled slag or ciuder. For the estimation of the total carbon, the following methods have been generally adopted:—

1. Combustion of a weighed quantity of the iron in a porcelain tube in a stream of oxygen. The chief objection to this process is the very high temperature required.

2. Combustion of the carbon in the residue left when iron is dissolved by the aid of iodine in presence of water, but the length of time required for solution is a great objection to this method.

3. The total carbon is frequently estimated by dissolving the iron in a solution of copper chloride or sulphate. The chief defect in this otherwise excellent process is that unless the vessel containing the iron undergoing solution is kept very cool, a decided smell is perceptible, probably indicating the evolution of hydrocarbons. The time required for solution is also rather long.

4. Weyl's method for determining the total carbon is a modification of the above process, using a galvanic current to accelerate the solution of the iron, but even in this case it is difficult to prevent the evolution of gas from the iron.

5. Lastly, Wöhler's method consists in heating a weighed portion of the iron in chlorine gas, whereby the iron is volatilised as chloride; the residual carbon can then be submitted to combustion.

The author has undertaken a series of experiments with the view of avoiding some of these difficulties. His first desire was to secure a process by which silicon could be rapidly and easily determined in iron and steel, and at the same time distinguished from the slag, which is almost invariably mechanically intermingled to a greater or less extent. The total carbon is first determined by Wöhler's method. Another weighed portion of the iron is similarly treated in a stream of chlorine, whereby not only the iron, but the silicon, and probably the sulphur and phosphorus, are volatilised in the form of chlorides; the gas as it issues from the combustion tube is caused to bubble through water contained in a flask; the water in the flask immediately decomposes the silicon tetrachloride which is carried forward with the excess of chlorine, and soluble silica is formed. The water is afterwards evaporated to dryness, and the silica recovered and weighed. The presence of manganese is the source of a little difficulty, for its chloride is not sufficiently volatile to be easily removed from the contents of the boat by the stream of chlorine. Hence, when manganese is present, which is almost always the case, it is necessary to wash the residue in the boat before weighing. The residue, which consists of the total carbon and the slag, having been weighed, the weight of total carbon previously determined is deducted from this weight, the difference being the amount of slag. Thus in two simple and rapid operations, are determined, first the total carbon, secondly the silicon and slag.

The author gives a full account of the apparatus and the mode of procedure, and a selection of analyses to illustrate the results obtained by this process.

A similar process has been recommended by Drown and Shimer since the present paper was written. They quote results which in the main agree with those of the author, the only difference being that they do not seem to consider the presence of cinder in pig-iron as fully established. From the results of the author's experiments there can be very little doubt on this point. D. B.

**Estimation of Arsenic in Copper.** By A. H. SEXTON (*Chem. News*, 45, 255).—The author gives the results of his own experience with the various methods in use for the estimation of arsenic in copper, and of a method which he has devised and found to give accurate results:—

1. *Separation by Sulphuretted Hydrogen in an Alkaline Solution.*—This method is fallacious, inasmuch as copper precipitated in this manner always carries down with it a portion of the arsenic.

2. Abel and Field's method is based on the precipitation of the arsenic as lead arsenate, by means of lead nitrate and ammonia and

ammonium carbonate, the lead arsenate being subsequently decomposed with oxalic acid, the arsenic precipitated as sulphide, and finally weighed as ammonio-magnesium arsenate. This method gives results always and often considerably too low, the arsenic apparently not being completely precipitated in the first instance as lead arsenate.

3. *By Precipitation as Basic Iron Arsenate by Ferric Salt and Ammonia.*—This method gives results far less satisfactory than the preceding. The arsenic was never completely precipitated even in presence of a considerable excess of iron, sometimes as much as 10 per cent., rarely less than 3 per cent. of the arsenic remaining in solution.

4. *By Precipitation as Basic Iron Arsenate by means of Sodium Acetate.*—After repeated experiments, the following method was devised: The copper is dissolved in nitric acid, a small quantity of solution of ferric nitrate added, the solution nearly neutralised with soda, and excess of sodium acetate added. It is then heated to boiling, and filtered as rapidly as possible; the precipitate, after being well washed, is dissolved in hydrochloric acid, the solution made alkaline with ammonia, saturated with sulphuretted hydrogen, and filtered from the precipitated iron sulphide. The filtrate is acidified with hydrochloric acid and allowed to remain in a warm place for some time. The arsenic and antimony sulphides are filtered off, and dried at 100°; and the precipitates after complete removal from the paper into a small beaker, are treated with fuming nitric acid, a few drops of hydrochloric acid being added as soon as the action has ceased. The liquid is then diluted, and filtered, and the arsenic is precipitated as ammonio-magnesium arsenate, and weighed as usual. If the precipitated sulphides cannot be perfectly removed from the filter-paper, the latter must be treated with nitrohydrochloric acid, filtered, and the filtrate added to the nitric acid solution. This method has been found to give accurate results, and each stage of the process has been carefully investigated. It requires, however, some special precautions. When the sodium acetate is added the colour should change from pale blue to dark green; this shows that the solution has been sufficiently neutralised. If the solution be now left boiling (sometimes when it is not) a greenish-white precipitate of basic copper acetate falls. This can generally be removed by adding a few drops of hydrochloric acid; but in cases where it has separated on the surface or where it will not readily dissolve, it is best to throw away the solution and begin again. The precipitate should have the dark red colour of ferric acetate; if it is paler, it is due either to there not being sufficient iron, or to the co-precipitation of some basic copper acetate. The filtrate should be blue or pale green; sometimes it is dark green and turbid from the presence of iron acetate carried through the filter; in that case the first portions must again be passed through the filter. The precipitate must be washed until it is free from copper. If, on dissolving it in hydrochloric acid, the solution is at all green, it must be neutralised, a little more sodium acetate added, and the iron and arsenic reprecipitated. It was found that with 1.5 parts of iron to 1 of arsenic the precipitation was complete. In order to make sure, it is well to add about twice as much iron as is expected there is arsenic present.

Then, even if a little iron remains unprecipitated, all the arsenic will be thrown down. Since copper sulphide retains so much arsenic, it might be expected that iron sulphide would act in a similar manner, but it does not; if there be no copper present, the precipitate is quite free from arsenic; but if copper is present, a considerable quantity of arsenic may be retained. Hence the importance of thoroughly washing the acetate precipitate and reprecipitating if necessary. The antimony will be in the filtrate from the ammonio-magnesium precipitate, and may be estimated by Abel and Field's method, fuming nitric acid being preferable as the oxidising agent. The arsenic may also be readily estimated by precipitating with ammonium molybdate, redissolving in ammonia, and precipitating as ammonio-magnesium arsenate; but in this method the antimony must be estimated in a separate portion, and that can only be done by one of the methods (2 or 4) previously described. D. B.

**Estimation of Carbonic Anhydride in the Atmosphere.** By T. MASCART (*Compt. rend.*, **94**, 1389—1390).—The air in which the carbonic anhydride is to be determined is dried and introduced into one of the bulbs of an air thermometer, the other bulb of equal size being filled with dry air, and the two connected by means of a mercury manometer. The two bulbs are placed in a vessel of water maintained at a constant temperature, and the difference of the pressures of the two gases is noted when the level of the mercury in the reservoir is brought to a certain mark. The air to be examined is then withdrawn by a mercury pump, freed from carbonic anhydride by potash, and afterwards returned to the bulb. When the mercury is again brought to the same mark in the reservoir, the difference observed in the level corresponds with the carbonic anhydride removed, which is about 0.3 mm. for a pressure of 1 m. of mercury. By increasing the pressure at the time of reading, greater accuracy may be obtained: thus at a pressure of 4 m., the difference would be about 1.2 mm., the relative error being less than  $\frac{1}{100}$ .

The small quantity of air required in this method, only about 400 c.c., recommends it especially for the analysis of air during voyages, since small volumes of the air, about 500 c.c., may be sealed in glass flasks and brought to the laboratory for analysis.

L. T. O'S.

**Reducing Power of Beer and Wort.** By J. STEINER (*Bied. Centr.*, 1882, 414).—The rotatory power of wort or beer is dependent on the amounts of maltose and dextrin present; so that knowing the rotation and reducing power of a given volume of liquid, the percentage of sugar and dextrin may be calculated. Worts reduce Fehling's solution more than Knopp's. Beer reduces Sachsse's test more energetically than Fehling's. Analyses of starch-sugar by Fehling's solution give the highest results, Sachsse's the lowest; there is more than one reducing carbohydrate in wort and beer.

E. W. P.

**Analysis of Wine.** By F. JEAN and others (*Bied. Centr.*, 1882, 411).—Tannin and cenolin closely resemble one another, and the latter not only combines with animal membranes, but behaves towards

iodine solution like tannin. Upon this property, the author bases his method for the estimation of œnolin and œnotannin. The method is not described, but the percentages of these two compounds in various wines are given. E. W. P.

**Artificially Coloured Red Wines.** By P. PASTROVICH (*Ber.*, 15, 808).—The author finds that the presence of magenta in a red wine may be easily detected by shaking up the wine with coarsely-powdered manganese dioxide, leaving it at rest for a quarter of an hour, and filtering. A red coloration of the filtrate serves to indicate the presence of magenta. As already shown by A. Facen (*Zeits. Anal. Chem.*, 9, 21), natural red wine, when so treated, yields a colourless filtrate, and the author has also found that several other vegetable colouring matters are decolorised when so treated; this bleaching being due in all probability to an oxidation, inasmuch as the colour is restored by treating the solution with zinc and sulphuric acid.

P. P. B.

**Official Benzoic Acid.** By C. SCHNEIDER (*Arch. Pharm.* [3], 20, 401—413).—The author herein reviews the work done by Schacht and others, with the view of ascertaining the origin of benzoic acid, whether it be prepared from Siam benzoïn or from other sources. The method adopted by Schacht (this vol., p. 339) is not completely satisfactory, as the presence of cinnamic acid has a considerable influence on the reduction of the permanganate. Vanillin, which is added to benzoic acid prepared from toluene, &c., to produce the peculiar odour of benzoic acid from Siam gum, also acts powerfully in reducing permanganate. Schlickum examines benzoic acid for purity by means of ammoniacal solution of silver nitrate; but Schneider considers the process incapable of determining the genuineness of the Siam acid. The quantity of acid which can be sublimed from gum benzoïn of different localities is given. E. W. P.

**Behaviour of Official Benzoic Acid towards Potassium Permanganate.** By E. SCHÄER (*Arch. Pharm.* [3], 20, 425—430).—Benzoic acid from various sources was treated with acid and alkaline permanganate. It was found that the reducing action of genuine benzoic acid occurs in acid or alkaline solutions, and the reduction is greater than that of acids from other sources. In alkaline solution the non-official acids produce only a green coloration. Benzoic acid, separated from the gum by lime, resembles non-official acid in its feeble reducing power. Cinnamic acid also reduces permanganate, thus closely resembling sublimed benzoic acid: hence toluene benzoic acid mixed with cinnamic acid may be mistaken for the genuine substance. E. W. P.

**Aræometric Estimation of Fat in Skim-milk.** By F. SOXHLET (*Bied. Centr.*, 1882, 407—409).—As the aræometers are incapable of estimating the fat in skim-milk when it falls below 1·1 per cent., as the ethereal solution of fat will not then separate, it is recommended to add 0·035 per cent. of an alcoholic solution of potassium stearate to the milk, in the proportion of 200 c.c. milk to 20—25 drops of the solu-



tion, whereby the whole of the fat may be removed. A table of the sp. gr. of skim-milk containing 0·16—2·1 of fat is given. The ethereal fat solution does not separate nearly so well from boiled as from un-boiled milk.

E. W. P.

**Specific Gravity of Wax, Ceresin, &c.** By E. DIETRICH (*Arch. Pharm.* [3], 20, 454).—The following is a table of the sp. gr. of wax, together with various substances employed to adulterate it:—

Cera alba .....	0·973	Colophon.gallicum	1·104—0·105
„ flava.....	0·963—0·964	Oleum cacao fil-	
„ japonica ..	0·975	tratum.....	0·980—0·981
Ceresin, white ..	0·918	Paraffin.....	0·913—0·914
„ hf. white	0·920	Res. Pini depurat.	1·045
„ yellow..	0·922	Sebum bovinum.	0·952—0·953
Ozokerite (crude)	0·052	„ ovillum..	0·961
Cetaceum.....	0·960	Stearin .....	0·971—0·972
Colophon. Amer.	1·108		

## Mixtures.

Yellow wax.	Yellow ceresin.	Mixture.
Sp. gr. 0·963.	Sp. gr. 0·922.	Sp. gr.
80 parts	20 parts	0·957—0·958
60 „	40 „	0·950
40 „	60 „	0·937
20 „	80 „	0·931
White wax.	White ceresin.	Mixture.
Sp. gr. 0·973.	Sp. gr. 0·918.	Sp. gr.
80 parts	20 parts	0·962
60 „	40 „	0·957
40 „	60 „	0·938
20 „	80 „	0·932

E. W. P.

**Examination of Chocolate.** By E. HERBST (*Arch. Pharm.* [3], 20, 452—454).—The adulteration of chocolate with suet can be readily detected by extraction with ether. Cocoa fat melts at 27—31°, whilst suet melts at 34—37°; moreover, pure cocoa fat dissolves easily and clearly in two parts of ether; the presence of suet renders the solution turbid. The presence of sesame oil, added in small quantities (4 per cent.) to produce a smooth shining fracture, is not readily detected. Sugar must be estimated in the residue after removal of oil. Ash should not exceed 2 per cent. Microscopical search must be made for flour, sago, chicory, &c. Crude cocoa contains in the average 50 per cent. fat; therefore, if the chocolate is normal and pure, the fat must equal half the weight of the chocolate less that of the sugar, after the removal of sugar by 50 per cent. alcohol as above referred to.

E. W. P.

**Prollius' Method for the Estimation of Alkaloids in Cinchona Bark.** By J. BIEL (*Arch. Pharm.* [3], 20, 350—356).—

Prollius' method, extraction with ether and ammonia, or alcohol and chloroform, do not give exact results; comparative experiments, employing as a check analysis, one made according to Kissel's and Mons' process, showed very great errors, which amount in some cases to as much as 30 per cent. of the total alkaloids. Investigation showed that the maceration of the bark should be continued for four hours, and no longer. No account is taken of the alkaloids dissolved in the filtrate and wash-waters, and this constitutes a considerable error, to avoid which 100 grams of the ethereal solution are to be evaporated, the residue dissolved in acid and hot water, cooled, filtered from resin, and the alkaloids are then to be precipitated by dried sodium carbonate from the filtrate. The mixture is then evaporated to 20 c.c., the precipitate collected in a tared filter, and weighed. All the wash-waters are to be extracted by chloroform, and the chloroform evaporated. This modification obtains nearly the whole of the total alkaloids, as stated by Kissel (this vol., 897). E. W. P.

**Examination of the Root of *Berberis Aquifolium*, v. *Alpens*, "Oregon Grape Root."** By H. B. PARSONS (*Pharm. J. Trans.* [3], 13, 46—48).—In the roots of the barberry are found, beside other substances, two alkaloids, berberine and oxyacanthine, to whose presence the efficacy of these roots in cases of fever may be ascribed. Berberine forms brown-coloured salts with sulphuric, hydrochloric, nitric acids, &c., whilst the other alkaloid is decomposed by nitric acid, forming a resin. A list of reactions with various reagents and solvents is given. The roots of *Berberis* may easily be distinguished from those of *Hydrastis canadensis* by the presence of hydrastine, which is present, together with berberine, in the *Hydrastis*, but is absent in the barberry. The following is an approximate analysis of the *Berberis* :—

Moisture.....	6.08
Ash, soluble in water.....	1.63
„ insoluble in water.....	2.08
	3.71
Fibre.....	23.33
Albuminoids insoluble in water and alcohol ....	3.15
„ soluble in alcohol, insoluble in water	1.68
	4.83
Berberine ( $C_{20}H_{17}O_4$ ).....	2.35
Oxyacanthine ( $C_{16}H_{23}NO_6$ ) ? ( $C_{32}H_{46}N_2O_{11}$ ) ?.....	2.82
Black substance with oxyacanthine.....	0.23
Resin, insoluble in ether, soluble in alcohol.....	1.91
Sugar (traces), acids (?) colours.....	4.55
Ether extract (wax).....	1.36
Gum and yellow colouring matter.....	5.36
Starch isomerides by titration.....	18.05
Extracted by acids and alkalis.....	25.22

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 100.000

E. W. P.

**Forensic Chemical Determination of Gelsemine in Animal Liquids and Tissues.** By E. SCHWARZ (*Pharm. J. Trans.* [3], 13, 148—150).—The author in this paper does not seem to recognise any difference between *æsculin* and *gelsemic acid*, as is shown to exist by Wormley, and he gives a detailed account of the different reactions with reagents when various alkaloids are employed, whereby *gelsemine* may be detected. The final colour produced by *strychnine*, sulphuric acid, and an oxidising agent, is brick-red, while with *gelsemine* the colour is green; sulphuric acid containing iron shows no reaction with *gelsemine* or *strychnine*, but a blue-violet with *quebrachine*; *Froehde's reagent*, with *gelsemine*, brown changing to green; *strychnine*, no change; *geissospermine* and *quebrachine*, blue; sugar and sulphuric acid, with *gelsemine*, cherry-red; fats, biliary acids, *aconitine*, *codeïne*, and *delphinidine*, the same; *strychnine*, no colour; *quebrachine*, deep cherry-red; *iodic acid* in sulphuric acid, *gelsemine*, *strychnine*, rose-coloured; *brucine* and *aspidospermine*, brick-red; *quebrachine*, dark-violet. Several other tests are given. *Æsculin* (*gelsemine*?) may be found in all organs; and *gelsemine* in the stomach, intestines, blood, and liver. Both pass rapidly from the stomach into the blood, and thence into the urine. *Gelsemine* is distinguished from *quebrachine* by not being extracted by chloroform from acid solutions; the reaction with *Froehde's reagent* by sulphuric acid containing iron, and by the absence of *æsculin* (?) from *quebracho bark*. E. W. P.

**Estimation of Urea by Sodium Hypobromite.** By C. ARNOLD (*Arch. Pharm.* [3], 20, 356—361).—As the methods for the estimation of urea are all erroneous, in that the absolute quantity of urea is not determined, the results as obtained by *Hüfner* and *Simpson's apparatus* were compared, and it was found that the decomposition of urea is greatly facilitated by an excess of alkali in the solution: an excess of bromine above 45 c.c. per litre ceases to raise the results when the bromine solution contains a definite amount of alkali; an excess of alkali is more advantageous than an excess of bromine; *Hüfner's apparatus* yields as good results as *Simpson's* only when the solution contains 1 per cent. urea. In cases where pure urea is to be estimated, the *Bunsen-Salkowski process* is the best. Compared with a direct estimation of urea by soda-lime, *Hüfner's method* yields results 9 per cent. too low. Comparisons of nitrogen in urine estimated by soda-lime, *Liebig-Pflüger* and *Hüfner-Knop's method*, the soda-lime results being the standard, show that *Liebig's process* gives a result more than 0.5 per cent. too low, and *Hüfner's* nearly 7 per cent. below the true quantity. It is therefore evident that *Hüfner's method* is not adapted for exact scientific work. E. W. P.

**Researches on the Behaviour of Ferric Chloride to Albumin.** By G. BUCHNER (*Ann. Pharm.* [3], 20, 417—425).—Iron albuminate is by no means of constant composition; all its constituents vary in quantity according to the treatment of the original substance; boiling with water, heat, &c., all affect it. At times the iron is in excess, and appears to be present as hydrated ferric oxide; the chlorine may also be in excess, perhaps as free hydrochloric acid or combined with albu-

min, the iron being then combined as hydroxide, also with the albumin; the albumin, therefore, appears to play the part of an acid and also of a base. Some of the elements lose their identity when in this condition of combination. If albumin is digested with powdered iron, a brownish liquid is formed possessing all the properties of dialysed iron albuminate; a similar result is obtained if ferric hydrate is employed, but the percentage of combined iron is different.

E. W. P.

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## Technical Chemistry.

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**Wilde's Chloride of Silver Gelatin-plates for Diapositives.** (*Chem. Centr.*, 1882, 350.)—It has for some time been recommended to produce diapositives by preparing direct copies on chloride of silver gelatin-plates. Emulsions are made with an excess of silver, that patented by Haakman being one of the best. It consists of 5 grams gelatin, 1.5 silver nitrate, 0.5 calcium chloride, 0.5—1.0 citric acid, and 100 c.c. water. The difficulty is the want of durability of the plates, which, owing to an excess of silver, change very quickly. Wilde has overcome this objection, and the plates may now be kept in a dark place for over a year. The sensitiveness to light is relatively large,  $1\frac{1}{2}$  to  $2\frac{1}{2}$  hours' exposure under a negative being sufficient. It is necessary to over-expose the pictures, as they reduce on fixing. It is a characteristic fact, that, on fixing, these plates assume a purple tinge without the use of a gold bath. D. B.

**Pure Carbons for the Electric Light.** By JACQUELAIN (*Compt. rend.*, 94, 873—876).—The paper describes the processes of purifying gas-retort carbon by treatment with chlorine-gas, with fused caustic soda, or with hydrofluoric acid. The author finds that a certain natural graphitoid carbon from Siberia acquires by purification a luminous power double that which it possesses in its natural state, and one-sixth greater than that of pure artificial carbons. R. R.

**Hygienic Significance of Drinking Water.** By M. BARTH (*Bied. Centr.*, 1882, 361).—Water used for drinking may serve as a means of conveying germs of infection. These germs accompany the liquid from cesspools, &c., which liquid nourishes their growth. Putting aside the possibility of the conveyance of infection, the consumption of such water must be considered as dangerous to health, being a centre of decomposition, or else containing those constituents which will make it such. Contaminated water must contain nitrogenous matter, or else non-nitrogenous organic matter, together with nitrogen in inorganic combination. Water which contains no oxidisable nitrogenous matter, but is rich in nitrates, must not be pronounced as healthy, and must be regularly examined. Chemical examination of water should also be supplemented by microscopical examination. E. W. P.

**Disinfection by the Aid of Hot Air.** By R. KOCH and G. WOLFFHÜGEL (*Chem. Centr.*, 1882, 383).—The following are the conclusions arrived at:—1. Poreless bacteria cannot exist in hot air having a temperature of  $100^{\circ}$  and after  $1\frac{1}{2}$  hours' exposure. 2. To kill spores of fungi an exposure of  $1\frac{1}{2}$  hours at a temperature of  $110$ — $115^{\circ}$  is required. 3. Spores of bacilli are destroyed on exposure to  $140^{\circ}$  for three times this period. 4. In the case of hot air, the temperature penetrates into the objects to be disinfected very slowly: goods of small dimensions, *e.g.*, small bundles of clothes, pillows, &c., are not disinfected after heating for 3—4 hours to  $140^{\circ}$ . 5. Exposure to a temperature of  $140^{\circ}$  for three hours is more or less injurious to most articles. D. B.

**Difference in the Action of Solution of Carbolic Acid in Oil and in Water.** By G. WOLFFHÜGEL and G. V. KNORRE (*Chem. Centr.*, 1882, 367).—In his treatise on antiseptics, Koch observes that solutions of carbolic acid in oil are inferior to aqueous solutions in their disinfecting action. The authors have made it their object to ascertain the cause of this peculiarity. The action of a disinfectant cannot be regarded as perfect unless it enters into all parts of the objects to be preserved and penetrates into the micro-organisms adhering to and living in the same. As water has a greater power of increasing capillarity than oil, it penetrates with greater ease; oil in penetrating into substances containing water has to contend with obstacles. It is, however, possible that by bringing aqueous and oily solutions together, an interchange between the dissolved constituents takes place, inasmuch as they are soluble in both liquids. On investigation, it was found that the carbolic acid from carbolic oil is not given up to water as freely as that from carbolic water to oil, a circumstance which is explained by the greater solubility of carbolic acid in oil. To what extent this peculiarity of the oil and its inferiority in penetrating into porous solids and mixing with liquids is attributable as the cause of the inactivity of carbolic acid in oily solutions cannot be estimated, as it has not been determined how oil and water behave as regards giving up carbolic acid to micro-organisms. Oil should not be used as a solvent for carbolic acid in cases where it is desirable that the fungi adhering to or living within watery, solid, and liquid bodies, should be destroyed within 24 hours after treatment. D. B.

**Portland Cements.** By H. LE CHATELIER (*Compt. rend.*, 94, 867—869).—The principal constituent of Portland cement, and the most active agent in its setting is the calcic silicate,  $\text{SiO}_2 \cdot 2\text{CaO}$ . This by contact with water produces, among other compounds, a substance crystallising in hexagonal plates, and playing the chief part in the hardening of the cement; but the author has not yet been able to determine its composition. Calcic aluminates and ferrates are also frequently present in Portland cements. R. R.

**Malleable Cast Iron.** (*Chem. Centr.*, 1882, 366).—The manufacture of malleable cast iron depends on two operations: (1) pouring the cast iron into the moulds and (2) removing part of the carbon

contained in the castings. This is conducted in so-called tempering furnaces, wherein the castings are brought into contact with substances containing oxygen and heated to redness. The result is the formation of a very tough material poor in carbon. The castings contained in cast-iron vessels are placed on a layer of oxidising substances, and the intervening spaces filled up with the latter. Oxide of zinc, hammer scale, brown and red iron ore are used for this purpose, mostly the latter. The operation lasts 24 to 96 hours, and depends on the dimensions of the iron to be tempered and the degree of tempering; with regard to the latter, the limits are within a wide range, as with a correct formula of mixing it is possible to absorb the whole of the carbon. It is best to use iron free from manganese and containing amorphous carbon, *i.e.*, white pig iron. The tempered iron forms an excellent material, and compares favourably with malleable iron with regard to firmness. It can be worked and polished with file and chisel, or forged and welded at a moderate red heat.

D. B.

**Preparatory Treatment of Manganese Ores for the Production of Ferromanganese and Crude Manganese in the Blast-Furnace.** By A. LEDERER (*Chem. Centr.*, 1882, 351).—In the preparation of ferromanganese and crude manganese, manganese ores are used, in which the manganese is present as manganese dioxide,  $MnO_2$ , or its hydrate,  $MnH_2O_3$ . In the upper part of the blast-furnace, by the action of ascending currents of gas containing carbonic oxide, these ores liberate a portion of their oxygen, being converted into manganic oxide,  $Mn_2O_3$ , or manganoso-manganic oxide,  $Mn_3O_4$ , whilst a corresponding quantity of carbonic oxide is transformed into carbonic anhydride. This operation is accompanied by a considerable rise in temperature, so that a strong upper fire is formed in the blast-furnace, through which the sides and interior of the furnace are rapidly destroyed, whilst the hot stream of gas being largely contaminated with carbonic anhydride cannot be utilised. This difficulty may be overcome by reducing the ores to lower oxides,  $Mn_2O_3$  or  $Mn_3O_4$ , using a process which consists in subjecting the ores in closed vessels to the action of a superheated current of air, or by allowing a current of air containing carbonic oxide to act on them at a temperature of about  $300^\circ$ . The first process has the advantage that the liberated oxygen mixes with the hot blast, and therefore increases the temperature in the lower part of the furnace, the result being a more economical consumption of heat; but the process requires large apparatus, a long time of action, and a temperature not less than  $700^\circ$ . The second process can be effected by the aid of a simple form of apparatus. A furnace (shaft or crucible furnace) is required, in which the ores are brought in contact with the reducing gases. The most suitable furnace is a crucible furnace with inclined bed, the gases entering at the lowest part, whilst the ore is moved in a direction opposite to the current of gas. As reducing agent, generator gases or flue gases from the blast-furnace may be used.

D. B.

**Effects of Compression on Steel.** By LAN (*Compt. rend.*, 94, 952—954).—Steel, by compression as in Whitworth's process, becomes richer in combined, and poorer in uncombined carbon, the total quantity remaining of course the same. As regards hardening, temper, and combined carbon, the effects of compression on cast iron and steel are the same as those of sudden cooling in casting. R. R.

**Plating of Tin, Brass, White Metal, or Copper Utensils with Platinum.** (*Chem. Centr.*, 1882, 384.)—The clean metallic surface is planished and rubbed with a solution of 1 part platinum chloride, dissolved in 15 parts alcohol and 50 parts ether, and when dry polished in a warm place with a dry cotton or woollen cloth. Bad places in platinum platings may be made good in a similar manner. The coating resembles steel in appearance, and imparts to bronze, brass, or copper utensils a fine platinum surface. D. B.

**Cleaning of Dull Gold.** (*Chem. Centr.*, 1882, 367.)—Take 80 grams calcium hypochlorite, 80 sodium bicarbonate, and 20 sodium chloride, and treat the mixture with 3 litres of distilled water. The whole is then poured into well corked bottles and kept for use. To cleanse the goods they are put in a basin and the mixture poured on to them until they are covered by it. After some time they are taken out, washed, rinsed in alcohol, and dried in sawdust. The articles have then the same appearance as if new. D. B.

**Valuation of Crude Spirit.** By M. MAERKER (*Bied. Centr.*, 1882, 415).—Fusel oil is always obtained during the distillation of ethyl alcohol, but the extent to which it occurs is dependent on the crude material employed, on the treatment of that material, and on the yeast. E. W. P.

**Clarification of Must in the Manufacture of Champagne.** By F. JEAN (*Compt. rend.*, 94, 800—802).—The author determines the quantity of tannin rendered insoluble by the albuminoid matters in the must, and also the quantity required to precipitate the whole of the gelatin introduced by the usual addition of isinglass. The former determination he effects by neutralising 10 c.c. of the must with dilute solution of sodium carbonate, adding some bicarbonate, and ascertaining the volume of iodine solution absorbed by the œnogallic acid and extractive matters. He then similarly ascertains the volume of iodine absorbed after the addition of a certain proportion of pure tannin to the must, and this gives the quantity of tannin rendered insoluble by the albuminoid matters in the must. On the other hand he finds that 100 parts of isinglass render insoluble 82·8 parts of tannin. The quantities of isinglass and of tannin required for the clarification of the must may then be determined. R. R.

**Analysis of Wine from Jacquez Grapes.** By J. BOUSSINGAULT (*Bied. Centr.*, 1882, 430).—Alcohol 9·7 per cent., total acids 0·597, VOL. XLII. 4 g



tartrac 0.054, sugar traces, tannin 0.15, dry matter 3.98, glycerol 0.8, succinic acid 0.2, ash 0.3, alkalis in ash 0.162, sp. gr. 0.989.

E. W. P.

**Analysis of various Munich Yeasts.** By REISCHAUER (*Bied. Centr.*, 1882, 432).

**Preservation of Yeast.** (*Bied. Centr.*, 1882, 432).—Good yeast should be twice well washed with ice-cold hard and spring water, then dried and well pressed. This mass is then to be well mixed with malt-meal dust, and preserved in closed jars in ice cellars.

E. W. P.

**Preparation of Dextrose from Starch.** By E. DELARNE (*Bied. Centr.*, 1882, 413).—Instead of employing sulphuric acid, which imparts an unpleasant flavour to the dextrose, the starch is to be heated with  $\frac{3}{1000}$  of its weight of oxalic acid for 45 minutes at 140°.

E. W. P.

**Method of obtaining Sugar from Molasses.** By R. WACHTEL (*Bied. Centr.*, 1882, 430).—Digest together 100 grams molasses (51.6 per cent. polar.), 66 grams pure quicklime, 200 c.c. spirit, 45° Zr. The precipitated calcium saccharate is to be decomposed by carbonic anhydride, and magnesium carbonate is to be added. On adding lime and spirit to the filtrate, very pure calcium saccharate separates.

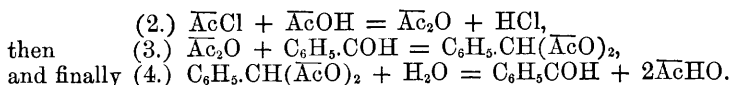
E. W. P.

**Variation in the Coefficient of Purity of Juices and Syrups, a Consequence of Sp. Gr.** By H. PELLET and C. BRÜNINGS (*Bied. Centr.*, 1882, 416).—Estimation of the purity of a syrup is affected by the sp. gr.; for a diluted juice shows a different percentage of sugar from the same when undiluted. To obtain correct results in the comparison of various juices, they should all be diluted to the same extent.

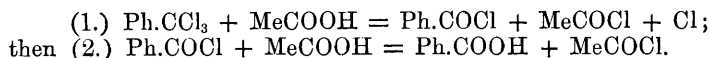
E. W. P.

**Production of Benzoic Acid and Bitter Almond Oil from Toluene.** By A. T. JOB (*Pharm. J. Trans.* [3], 13, 61).—This process, which has been patented by E. Jacobsen, is dependent on the formation of di- and tri-chloromethyl-benzene from chlorine and toluene at a high temperature. The action of water or potash on the first compound produces benzaldehyde; whilst from the second benzoic acid is formed. Jacobsen states that the action of glacial acetic acid on dichloromethylbenzene in presence of zinc chloride, yields benzaldehyde, acetic chloride, and hydrochloric acid; he also states that zinc oxide may replace the chloride. The author when repeating the experiment found that a red liquid was formed possessing a powerful odour, different from that of benzaldehyde; crystals were deposited of the composition  $\text{CHPh}(\text{AcO})_2$ . The reaction is supposed to occur as follows:—(1.)  $\text{Zn}(\text{AcO})_2 + \text{CHPhCl}_2 = \text{CHPh}(\text{AcO})_2 + \text{ZnCl}_2$ . When zinc chloride is present, we have the

acetic chloride produced in the primary reaction, decomposing the acetic acid.



Therefore, to prevent the formation of the crystals referred to, it is advisable to add from time to time a little water. The reaction which results in the formation of benzoic acid is—



The difficulty of the process consists in obtaining a sufficient amount of trichloromethylbenzene free from the dichloro-compound.

E. W. P.

**Preparation of Solid Fatty Acids.** By A. MÜLLER-JACOBS (*Chem. Centr.*, 1882, 384).—Oleic and erucic acids, or their natural glycerides, such as cotton-seed oil, rape-seed oil, olive oil, sunflower oil, and train oil, are cooled to a temperature of  $+6^\circ$  and treated with 30–40 per cent. of cooled sulphuric acid of sp. gr. 1·823–1·826. The temperature of the mixture increases during this operation, and when it has reached  $35^\circ$  twice the volume of water is added, and the whole kept at rest for 24 hours. A sulphonic acid is thus obtained which is decanted from the solution containing sulphuric acid and glycerol and boiled with water. The acid splits up into sulphuric acid and a mixture of a fatty acid and hydroxyoleic acid soluble in alcohol: the solid fatty acid crystallises out on cooling, and after being separated by filtration and pressure, is purified with alcohol, light petroleum, &c., or by distillation. It melts at  $70\cdot6^\circ$ , resembles stearic acid, and is a very useful mordant, taking the place of the usual oil mordant for Turkey-red dyeing, when converted into an alkali salt. It is used for candle making. The liquid portion of the mixture is hydroxyoleic acid, which may be used for soap making.

D. B.

**Change of Milk-Casein.** By E. MEISSL (*Ber.* 15, 1259–1264).—It has been shown in the author's laboratory that cow's milk under suitable conditions can, by warming, be kept for a year in closed flasks, and that such milk does not differ in colour, taste, reaction, and chemical analysis from freshly drawn milk. However, after some time a change sets in: for the fat, which separates out on the surface of the flask, has a tallow-like, rancid taste, and finally, the whole appearance of the milk is altered without coagulation. The fat thus separated on the surface as a kind of solid cream under which is a pale golden serum, whilst at the bottom a slight pulverulent precipitate separates out. The above-mentioned fat resembles ordinary butter fat which has become rancid; but its melting point is unaltered; the pulverulent precipitate has all the properties of freshly

precipitated casein. A more minute analysis of this preserved milk revealed the presence of the following constituents:—

(i.) Rancid fat; (ii) milk sugar, 4—5 per cent.; (iii) a substance resembling casein, 5 per cent.; (iv) a substance intermediate between albumin and peptone, 6—8 per cent.; (v) a substance having the properties of peptone; (vi) leucine, tyrosine, ammonia in very small quantities; (vii) aspartic and glutamic acids, traces. Notwithstanding a careful microscopic examination, no organised ferment could be discovered, so that the change cannot be considered to be due to the action of ferments, but rather to a long-continued interaction of the separate milk constituents. Fresh milk, after heating for two to three weeks at a temperature of 60°, behaves like this preserved milk; it becomes bitter to the taste, and loses the property of coagulating with acids. The author examined old milk cheeses, and found the same substances as in the milk, but in different proportions. It appears then, that by this long interaction the casein is converted for the greater part into peptone, and only traces of a crystalline decomposition-product; but, by putrefaction, less peptone and more of the crystalline substance are formed, the latter reaction being more energetic than the former.

V. H. V.

**Preservation of Milk.** By O. LOEW (*Ber.*, 15, 1482—1483).—This paper contains strictures on recent observations of Meissl (preceding abstract) on changes undergone by milk on keeping. These he referred to the long-continued interaction of the constituents, neither decay nor fermentation being observable. The author rejects this explanation because, when previously heated at 120° for some time, milk remains permanently unchanged. At the same time, he takes occasion to detail the following observations on a specimen of milk. This had been heated in the summer of 1872 for 40 minutes at 101°, and set aside until the autumn of 1880.

An examination disclosed the following facts:—The liquid (400 c.c.) was of a brownish colour; slightly acid; covered with a layer of fat; and containing a sediment (1.41 grams). The milk-sugar was found completely converted into lactose and glucose. The casein and albumin were entirely peptonised; the peptones, moreover, having undergone partial decomposition with formation of leucine and tyrosine, which were isolated. The sediment mentioned above, which occurred in hard fibrous masses, was boiled with potash; on neutralising the solution, tyrosine separated in characteristic needles, the yield being 90 per cent. of the original substance, which the author therefore regards as an anhydride of tyrosine.

C. F. C.

**Comparison of the Holstein and Swarts' Creaming Process.** By FRIEDLÄNDER and SCHMÖGER (*Bied. Centr.*, 1882, 398—400).—The yield of cream, as obtained by the two processes in experiments extending over two years is, on the average, the same, although at any one period there will be a difference between the two. As regards the yield of butter, at one time Swarts' produces the highest, at another the Holstein; Swarts' being lowest in April and May, and again lowest in December and February. Swarts' process gives the better

yield of cheese, 6.68 kilos. skim-milk producing 1 kilo. cheese, as against 1 kilo. cheese from 7.4 kilo. milk by the Holstein. The percentage of fat removed is higher at higher temperatures.

E. W. P.

**Employment of Lawrence's Cooler in the Creaming of Milk.** By H. v. PETER (*Bied. Centr.*, 1882, 401).—If the cream be removed from the milk after it has only been cooled for a short time, loss will be incurred, as the uncooled milk yields a larger supply of cream. If, however, the cooling, &c., is extended over 36 hours, then the yield from cooled and uncooled milk is alike. To obtain the best yield, the milk should not remain in wooden tubs, but in vessels of tinned iron.

E. W. P.

**Report of the Experimental Dairy at Kiel for 1880—1881.** By M. SCHRODT (*Bied. Centr.*, 1882, 402).—The best yield of butter from cows fed with cotton-cake occurred in November, the lowest in July, the average yield being 1 kilo. butter from 31.6 kilos. milk. Evening milk was richer in fat than morning milk, as also in total dry matter, and the sp. gr. varied from 1.0349 to 1.0285.

E. W. P.

**Preparation of Essence of Rennet.** By T. NESSLER (*Bied. Centr.*, 1882, 410).—The rennet cut up into small pieces is boiled in a flask with 1.5 litre soft water and 80 grams sodium chloride; after being allowed to stand for 22—24 hours, 0.2 litre alcohol is added, and the liquid is allowed to stand for three weeks. To clear the liquid, small pieces of filter-paper are introduced into the flask and left for some time; to this paper the slimy matter adheres, and is readily removed. One litre of this extract suffices to curdle 4000 litres milk.

E. W. P.

**Action of Rennet Ferment.** By A. MAYER (*Landw. Versuchs.-Stat.*, 27, 247—255).—This paper is a summary of a course of experiments on the coagulation of milk by rennet. The influence of temperature is considerable, a temperature of 37° is the most favourable; at 45° milk loses the property of coagulation, but it retains it as low as 25°, the process then occupies thrice the normal time. The quantity of rennet used is in inverse ratio to the time occupied by the process, and the addition of water to the milk has an injurious effect far out of proportion to the quantity added; but the same effect is not produced when the milk is left to coagulate naturally by souring. The fat contents of milk do not in any way influence the coagulation, nor does strong mechanical agitation prevent it, except that in the latter case the cake of cheese formed is not so homogeneous as when quietly deposited. A gentle warmth during the whole process is very beneficial. When casein is removed from milk by treatment with acetic acid, and the remaining fluid heated to 75°, the albumin left in it is precipitated. Addition of common salt in the proportion of about 0.9 per cent. accelerates coagulation, but if the quantity is much exceeded the beneficial effect is counteracted. Boric acid added in

such quantity as will neutralise the alkaline reaction is not hurtful to the process, but the addition of alkalis retards coagulation. The addition of rennet to milk which has begun to coagulate from the formation of lactic acid, hastens the process. The treatment of the rennet extract during its preparation is a matter of great importance. Light is very injurious, and especially so if there is free access of air, but air without light does not appear to act prejudicially; dust, dirt, or even the presence of bacteria of putrefaction does not appear to take away its power of coagulation. A rise of temperature to about  $66^{\circ}$  kills the ferment, which is also destroyed if the solution becomes alkaline, or if other organisms are present which change its acidity into alkalinity. The isolation of the rennet ferment in a state of purity being very desirable, the author experimented with various metallic salts, in order to precipitate it from the solution; the best effect was produced by zinc chloride, followed by a soluble calcium phosphate, but on the whole it was not satisfactory. Further experiments were made as to the difference between cheese produced from casein precipitated by acetic acid and that by use of rennet; the former it was found could be reconverted into a fluid possessing the properties of milk, the latter could not be so treated. The rennet coagulum also carries down with it more particles of fat, and the ash is considerably greater than that of casein coagulum. The ferment seems to exhaust itself in the process of coagulation, as the filtrate when added to fresh milk is inoperative. The author at one time thought it was due to its actual exhaustion, but now inclines to the opinion that it becomes entangled in the coagulum. J. F.

**Bark of Fraxinus Americana.** By J. M. BRADFORD (*Pharm. J. Trans.* [3], 13, 128).—A mixture of alcohol and water (1:4) is best adapted for extracting the bitter principle from the bark of the white or American ash; the alcoholic extracts are soluble in water, and ether removes from the bark a greenish fat, which changes to yellow-red when heated. H. M. Edwards also obtained a pungent resin from the same bark, but no tannin is removed by boiling with water.

E. W. P.

**Aniline Black.** (*Dingl. polyt. J.*, 244, 157—164.)—This paper gives a full account of the investigations carried on by Witz on the use of vanadium instead of copper in the preparation of aniline black. It was found that furniture cloth did not develop the black used as a ground colour, but produced a dull grey, whilst in some places the colour did not appear at all. The undeveloped parts were treated with a solution of vanadium and warmed gently, the result being the immediate appearance of the black. Witz quotes the following experiment as a proof of the importance of the action of vanadium as an oxidising agent for aniline black:—Badly developed pieces of cloth were blocked with a solution containing 0.01 gram vanadium in 1 litre of water, *i.e.*, ten times the quantity contained in the original printing colour. A uniform black was produced, and the pieces could be finished successfully, although they were more than 14 days old. In another case the black forming the ground exhibited a worse appearance. On examination it was found that the spotted parts con-

tained traces of ferric oxide. The cloth had been dyed with aniline black in a vat which had been used previously for printing with steam blue (prepared with ferrocyanide), and had not been washed out carefully. It was treated with vanadium, when a uniform black was produced. On investigation, Witz found that the presence of potassium ferrocyanide prevents the formation of vanadium black. The steam blue was composed of insoluble ferrocyanide of tin and soluble ferrocyanide of potassium. The latter produced a light grey colour which is not altered by dyeing, steaming, or chromatising. It is, however, a remarkable coincidence that whereas this salt, under certain conditions, retards the development of aniline black energetically, its acts in a reverse manner, and offers but little resistance when its proportions are increased. This change is most marked in the case of chromatised aniline black. The study of the action of alkaline ferrocyanides, as reserves for aniline black prepared with copper, in comparison with black prepared with vanadium, shows that potassium ferrocyanide thickened with dextrose resists vanadium black better than copper black. By replacing the copper sulphide with a corresponding quantity of copper sulphocyanide, the development of the black is retarded, although the result approaches that obtained with vanadium black. Ammonium thiocyanate also retards the formation of vanadium black, and it does this in the same way as a weak alkaline product. With 10—20 grams per litre, the action is noticeable, but with 80 grams per litre the oxidation is hindered very considerably. The action of potassium ferrocyanide, as a reserve under vanadium black, was tried. 10—15 grams per litre give a light grey, 100—120 grams a white, whilst 200 grams produce a greyish-violet colour, and with a further increase still darker shades are obtained.

In conclusion, Witz gives an analysis of basic slags obtained from blast furnaces in the Thomas-Gilchrist process. On an average, 1 per cent. of vanadium is found. It is shown that on treating the slag with hydrochloric acid, a solution of vanadium is obtained, which can be used without removing the impurities, as the quantity of vanadium required is so small that the impurities cannot affect the results obtained.

D. B.

**Croatian Bread.** By G. JANECK (*Chem. Centr.*, 1882, 266).—The author had occasion to examine bread recommended for use in cases of famine. It was prepared by baking a mixture of corn, maize, and beechwood flour, the latter being soaked in water. The bread was kept for 10 days and analysed. (No. 1.) The author also gives an analysis of new bread made from maize. (No. 2.)

	No. 1.	No. 2.
Water .....	35.73	53.63
Fat.....	0.41	1.36
Free acid (calc. as lactic acid) ....	2.34	traces
Dextrose and gum .....	4.50	4.66
Sugar.....	1.58	0.70
Protein substances .....	7.39	5.86
Cellulose .....	9.05	3.91
Other non-nitrogenous bodies—		
Soluble in $H_2O$ .....	5.76	4.40
Insoluble .....	31.50	24.10
Sodium chloride .....	0.41	0.43
Ash .....	1.09	0.89
Sand and clay .....	0.24	0.06

D. B.

**Penetration of Heat into Meat during Cooking.** By WOLFFHÜGEL and HÜPPE (*Chem. Centr.*, 1882, 267).—The authors used Kronecker-Meyer's maximum effluxion-thermometers for the determination of the maximum temperatures to which meat is exposed in the various modes of preparing it. On boiling pieces of meat weighing 3 kilos., the temperature after  $2\frac{1}{2}$  hours was  $92^\circ$  and  $96^\circ$ , according as the meat was placed directly into boiling water, or heated to boiling with cold water. A piece of ham weighing 4.5 kilos. was boiled for 4 hours, and showed a temperature of  $88^\circ$  in the interior. A piece of lamb weighing 3 kilos. had, during roasting, an interior temperature of  $92$ — $98^\circ$ . In a second series of experiments, the internal temperatures of tin boxes for preserving corned beef were determined. The boxes were put into boiling water, boiling solutions of salt ( $101$ — $104^\circ$ ), calcium chloride ( $108$ — $111^\circ$ ), and into a steaming pan ( $110$ — $113^\circ$ ). When the temperature of the bath was under  $106^\circ$ , that of the inner parts of the contents of the boxes was between  $87$ — $98^\circ$ , depending on the size of the boxes. Above  $106^\circ$  the temperature in the small boxes rose to  $102$ — $109^\circ$ , whilst in the larger boxes it remained stationary ( $72$ — $98^\circ$ ). This explains the fact that large boxes of American meat often become bad in places. D. B.

**Preservation of Vulcanised Caoutchouc.** By W. HEMPEL (*Ber.*, 15, 914).—In order to preserve caoutchouc stoppers and tubing, they should be kept in a closed jar, in which a vessel containing petroleum is placed. Caoutchouc stoppers which have become hard may be softened by exposure to the vapour of carbon bisulphide.

W. C. W.

## General and Physical Chemistry.

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**Change in Colour-tone of Spectral Colours and Pigments by Diminution in Intensity of the Light.** By E. ALBERT (*Ann. Phys. Chem.* [2], **16**, 129—160).—The analogy in the changes of spectrum colours and pigments is not complete. No conclusion can be drawn from the alteration of a homogeneous colour with regard to that of the corresponding pigment, the alteration in the latter being the resultant of the changes of the homogeneous colours composing the pigment.

The whole behaviour of homogeneous colours on diminution of light intensity is explained by the Young-Helmholtz theory, through the following assumption:—For a diminution in the intensity of various coloured light there is a different reduction of the sensitiveness, in such a way that the latter diminishes more slowly for rays of smaller than for rays of greater wave-length, no matter in what part of the spectrum they may be.

The author considers that the known facts in connection with this subject are a further confirmation of the Young-Helmholtz theory (compare Chodin (*Sammlung Physiologischer Abhandlungen von Preyer*, 1 Reihe, 7 Heft), Aubert (*Physiologie der Netzhaut*, 125), Helmholtz (*Phys. Optik*, 317); also Purkinje and Dove). T. C.

**Relation between the Molecular Refraction of Liquid Compounds and their Chemical Composition.** By H. SCHRÖDER (*Ann. Phys. Chem.* [2], **15**, 636—675).—From a careful comparison of the experimental determinations of Landolt and of Brühl, the author draws the following conclusions in regard to the molecular refraction of liquid compounds.

Contrary to the assumption of both Landolt and Brühl, the difference between the molecular refractions of compounds for equal differences in chemical composition is not constant, but increases distinctly, although slightly, with the atomic weight. The influence, therefore, of elementary atoms on the molecular refraction is not constant, but increases with the atomic weight of the compound, thus:—

	Molecular refraction.	Difference.
Formic acid, $\text{CH}_2\text{O}_2$ . . . . .	13·61 }	7·08
Acetic acid, $\text{C}_2\text{H}_4\text{O}_2$ . . . . .	20·69 }	7·32
Propionic acid, $\text{C}_3\text{H}_6\text{O}_2$ . . . . .	28·01 }	7·49
Butyric acid, $\text{C}_4\text{H}_8\text{O}_2$ . . . . .	35·50 }	

The influence of the components, and therefore of the elementary atoms of a compound on their molecular refraction bears a simple relation to one another. Thus the groups  $\text{CH}_2$ , CO,  $\text{OH}_2$ , and the  $\text{O}_2$  of acid carboxyl exert an equal influence on the molecular refraction.



tion of compounds containing them. Hence it follows that the atoms of H, C, and O (when combined with hydrogen in hydroxyl) possess the same "refraction-steres," whilst the diatomic O in CO has two refraction-steres. It is worthy of note that the formulæ which represent the refraction-constitution of saturated compounds are identical with those which the author had previously employed to represent the volume constitution. In every case of saturated compounds which has been examined, the elementary atoms have exactly the same number of steres for their volume constitution as for their molecular refraction. The stere in all the groups varies between 2·3 and 2·4.

As regards non-saturated compounds, a pair of doubly linked carbon-atoms (as in the allyl compounds) has twice the refraction-steres of a pair of carbon-atoms in saturated compounds.

The volume constitution and refraction-constitution of non-saturated compounds are no longer the same. The singly linked atoms of C, H, and O carry *one* stere, both in their volume constitution and in their refraction constitution, and a doubly linked oxygen-atom bears two steres in both cases. But whilst the volume-constitution of two doubly linked carbon-atoms is expressed by  $C_2^3$ , *i.e.*, three steres, that of the refraction constitution is represented by  $C_2^4$ , *i.e.*, four steres.

In aromatic compounds the carbon of phenyl ( $C_6H_5$ ) has twice as great an influence on the molecular refraction as in saturated compounds. In aromatic compounds, the volume constitution no longer agrees with the refraction constitution, for in the volume-constitution the 6 carbon-atoms of phenyl possess eight steres, whilst in the refraction constitution they have 12.

Brühl has drawn the conclusion that because the molecular refraction is greater by two units for each pair of doubly linked carbon-atoms than the sum of the influence of the elementary atoms according to the ordinary calculation, and, moreover, because the molecular refraction of aromatic compounds is greater by 6 units than calculation would lead us to expect, therefore there are three pairs of doubly linked carbon-atoms in benzene. The author thinks that this conclusion as regards the constitution of benzene is incorrect, even when considered from Brühl's point of view: for in non-aromatic compounds a loss of 2 atoms of hydrogen occurs for each double linking of the carbon-atoms, and consequently if Brühl be correct, there ought to be a loss of only 6 atoms of hydrogen for the three pairs of doubly linked carbon-atoms in benzene, whereas there is really a loss of 8 hydrogen-atoms. In the unsaturated compounds of the fatty series, the optical influence of the hydrogen which has been lost by each double linking of the carbon-atoms is completely compensated by the smaller lowering of the refractive power, whereas in the aromatic compounds the influence of the disposable hydrogen is not completely, but only three-fourths, counterbalanced by the increased action of the carbon.

The author considers that the heats of combustion (Thomsen), the volume-constitution (Schröder), and the refraction-constitution (Schröder) of aromatic compounds are all unanimously in favour of Ladenburg's prism, and not of Kekulé's hexagon as representing the constitution of benzene.

T. C.

**Galvanic Polarisation and Smee's Element.** By W. HALLOCK (*Ann. Phys. Chem.* [2], **16**, 56—86).—The usual view that the changes in the electromotive force of a Smee's element are due to the action of polarisation is correct. The electromotive force of the polarisation is by no means independent of the nature of the electrodes, nor are we at present in a position to calculate the polarisation from the heat evolved. The electromotive force of polarisation considerably exceeds that, which is necessary for the apparent decomposition, thus confirming the earlier views on this subject (compare *Wiedemann's Galvanismus*, **1**, 681 [1874]). T. C.

**Chemical Energy of the Voltaic Pile.** By D. TOMMASI (*Compt. rend.*, **94**, 1407—1410).—Joule and Favre have shown that there is a close relation between the energy of the voltaic pile and the heat developed by the chemical reactions taking place in the pile, so that the electromotive force of a couple will be proportional to the heat developed by the chemical action. Favre, however, states (*ibid.*, **69**, 39) that "the heat developed by the combustion of hydrogen in electrolysis is transmissible or not by the circuit, according to the nature of the compound supplying the oxygen necessary for this combustion." According to this, in a zinc-platinum couple with dilute sulphuric acid (Smee's element) the heat developed is 39 cal., but only 29·8 are transmissible by the circuit. Two of these couples, therefore, should not decompose water, for  $29\cdot8 + 29\cdot8 < 69$  cal. The author, however, has shown that decomposition does take place just as if the whole of the heat developed were transmissible,  $39 + 39 > 69$  cal. If the water in the voltameter is acidulated with hydrochloric acid decomposition of the water takes place more readily, the thermic equivalent being 66 cal. instead of 69 cal. But even in this case, according to Favre, it ought not to take place, for  $29\cdot8 + 29\cdot8 < 66$  cal.

If in the two Smee's elements graphite plates (previously heated to redness) be substituted for the platinum, decomposition takes place much more rapidly, and this is greatly increased when electrodes of gas-carbon of large surface are employed; yet, according to the views generally received, the chemical action of the pile ought not to be altered.

According to Favre, two zinc-platinum couples with dilute hydrochloric acid should not decompose water acidulated with sulphuric acid, whilst it should do so if acidulated with hydrochloric acid, for

$$\begin{aligned} 33\cdot4 + 33\cdot4 &< 69 \text{ cal. (H}_2\text{SO}_4\text{).} \\ \text{whilst } 33\cdot4 + 33\cdot4 &> 66 \text{ cal. (HCl)} \end{aligned}$$

This is in fact what actually takes place, but if graphite or, better, gas-carbon is substituted for the platinum of the couples, dilute sulphuric acid is decomposed. This cannot be explained on Favre's hypothesis, but is strictly in accordance with thermic considerations—

$$34\cdot2 + 31\cdot2 + 1\cdot4^* > 69 \text{ cal.}$$

Again, according to Favre, a zinc-platinum couple with hydrochloric

\* The electromotive force of an amalgamated zinc-couple is greater than that of a zinc-couple by about 0·7 cal.

acid should not decompose water acidulated with hydrochloric acid for

$$29.9 + 29.9 < 66 \text{ cal.}$$

It does take place, however, and even dilute sulphuric acid which absorbs 69 cal. is decomposed by a zinc and gas-carbon couple. If the water in the voltameter is acidulated with hydrobromic acid, this is decomposed and not the water, hydrogen being evolved at the negative, and bromine at the positive electrode. This is easily explained: for whilst water absorbs 69 cal. when decomposing, hydrobromic acid absorbs only 59 cal., and the author has previously drawn attention to the fact that of two compounds, that one is decomposed by preference which requires less thermic energy.

C. E. G.

**Electromotive Force of a Zinc-carbon Couple.** By BERTHELOT (*Compt. rend.*, **95**, 11—13).—The electromotive force of a zinc-carbon couple in dilute sulphuric acid varies greatly in consequence of polarisation, and the electrolytic effects which it can produce vary in exactly the same proportion. When the circuit is first closed, the electromotive force is greater than that of a Daniell cell in the ratio 1 : 1.29, but if the circuit remains closed, the electromotive force rapidly diminishes, and after 36 hours becomes less than half that of a Daniell. If the current is interrupted, the electromotive force gradually increases, but does not regain its original intensity. If, however, the carbons and porous cells are disconnected, well washed with water, and again set up, then on first closing the circuit the couple has exactly its original electromotive force. It is evident that a zinc-carbon couple cannot be used where a constant electromotive force is required. A zinc-carbon couple, when the circuit is first completed, will not decompose acidulated water, but if a zinc-cadmium couple is added, decomposition takes place. Two zinc-carbon couples will decompose potassium sulphate until polarisation has lowered the electromotive force below that of two Daniells.

C. H. B.

**Reply to Berthelot's Note "On the Electromotive Force of a Zinc-carbon Couple."** By D. TOMMASI (*Compt. rend.*, **95**, 81—82).

**External Work in a Closed Circuit.** By R. COLLEY (*Ann. Phys. Chem.* [2], **16**, 39—56).—The constant performance of external work in the circuit always determines the production of a new electromotive force, the amount of which is proportional to the work done, and that no matter whether the resistance changes or not.

In a closed circuit, there can be no electromotive force which does not correspond with the constant work of chemical or other forces.

T. C.

**Theory of the Equipotential Figures obtained by the Electrochemical Method.** By A. GUEBHARD (*Compt. rend.*, **95**, 29—30).—The formation of Nobili's rings is not due to a *permanent* electrical condition between the electrodes, but to a very short period of variable condition. The thickness of the deposit does not increase with the

time, but the extension of the rings ceases in a sharply defined manner. This metallic polarisation causes the production of a superficial inverse current. At the moment when the rings cease to increase, a permanent electrical condition is set up in the column of liquid of which the electrode forms the base, and each horizontal layer of this column separately obeys Lamé's equation. In order that any exchange may take place between the lowest layer of liquid and the electrode, it is necessary that the thickness of the polarising layer on the latter be proportional to the positive or negative values of  $\phi$  given by the equation  $\Delta_2\phi = 0$ . This affords further proof of the simple law which the author has previously established. C. H. B.

**Electrolysis of Hydrogen Peroxide.** By BERTHELOT (*Compt. rend.*, **95**, 8—11).—A dilute solution (3 grams per litre) of hydrogen peroxide undergoes electrolysis in two different ways. With sufficiently high electromotive force, oxygen and hydrogen are given off at the two electrodes, but with low electromotive force, such as that of a zinc-cadmium couple, only oxygen is given off, and no hydrogen is evolved at the negative electrode. Under these circumstances electrolysis resembles the spontaneous decomposition of the peroxide, but is accelerated by the action of the current. Either the hydrogen peroxide splits up into oxygen and water, or, more probably, a secondary reaction takes place, and the electrolysed hydrogen combines with undecomposed hydrogen peroxide, forming 2 mols. water, thus:  $H_2 + H_2O_2 = 2H_2O$ . The final result  $2H_2O_2 = 2H_2O + O_2$ , is exothermic, and develops + 43.6 cal., for  $H_2O_2 = H_2 + O_2$  absorbs - 47.4 cal., and  $H_2 + H_2O_2 = 2H_2O$  develops + 90.6 cal. This form of electrolysis can consequently be effected by any electromotive force however feeble.

When the electromotive force is equal to that of a Daniell cell, hydrogen is given off as well as oxygen, and the simultaneous evolution increases as the electromotive force increases. The electromotive force of a Daniell cell is the result of a reaction which develops + 49 cal., a quantity slightly higher than that absorbed by the decomposition of the hydrogen peroxide into its elements. The peroxide may possibly first split up into oxygen and water, the latter then undergoing electrolysis, but in this, as in all cases of electrolysis, only the initial and final conditions enter in the calculation of the minimum electromotive force required. For the same reason, the presence of dilute acid does not interfere with the result.

That both modes of electrolysis may take place simultaneously, as the author has already found in the case of ferrous and manganous sulphates (*Compt. rend.*, **93**, 760), is shown by the variations in the relative proportions of the oxygen and hydrogen evolved. With higher electromotive force, sufficient to decompose water, the decomposition becomes complex, and the ratio of hydrogen to oxygen evolved is increased in consequence of the electrolysis of the water present. C. H. B.

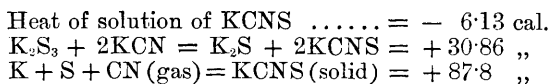
**Appearance of the Electric Arc in Vapour of Carbon Bisulphide.** By JAMIN and MANEVRIER (*Compt. rend.*, **95**, 6—7).—Two

vertical parallel carbons are arranged in the receiver of an air-pump, and the latter is exhausted until the arc no longer forms, but is replaced by the ordinary vacuum discharge. Vapour of carbon bisulphide is then introduced in quantity sufficient to increase the pressure by 50—60 mm. Under these circumstances a brilliant arc is formed, 50—60 mm. in height, with the shape of a horse-shoe, and surmounted by a long vertical flame. The arc has a pale green colour, and as the tension of the bisulphide vapour increases, the light becomes unbearably brilliant, but at this point the resistance becomes so great that the arc is frequently extinguished. If the receiver contains air, a cloud of sulphur is formed and deposited on the sides. If, however, all air has been removed, this cloud does not form, but a brown substance which turns black is deposited on the sides of the receiver. This substance is volatile, and has an odour resembling that of sulphur; it is possibly either carbon monosulphide or an allotropic modification of sulphur.

The spectrum of the arc under these conditions is very discontinuous, and consists of four very similar groups of channelled bands in the red, yellow, green and violet respectively, that in the green having by far the greatest intensity. The peculiar colour of this arc may possibly render it useful for lighthouses and signalling.

C. H. B.

**Heat of Formation of Thiocyanic Acid and of some Thiocyanates.** By JOANNES (*Compt. rend.*, **94**, 797—800).—The reaction between potassium trisulphide and cyanide requires nearly half an hour for its completion, the final result being represented by the equation  $K_2S_3 + 2KCN = 2KCNS + K_2S$ ; but from a comparison of the thermic changes with the amount of potassium cyanide formed during equal intervals, it would seem that some intermediate compound is first formed; this supposition is confirmed by the course of the reaction between potassium trisulphide and mercury cyanide, for although it takes about the same time as in the case of potassium cyanide before it is complete, the whole of the mercury is at once precipitated as sulphide, and the solution acquires an odour of hydrocyanic acid. The numbers obtained were as follows:—



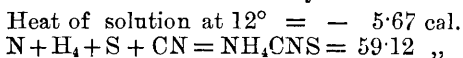
Heat of formation of thiocyanic acid—



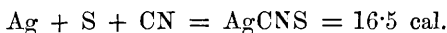
Heat of formation of sodium thiocyanate—



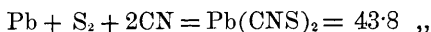
Heat of formation of ammonium thiocyanate. Its



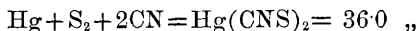
Heat of formation of silver thiocyanide—



Heat of formation of lead thiocyanide—



Heat of formation of mercury thiocyanate—



The heats of formation of the thiocyanates are intermediate between those of the corresponding iodides and bromides.

C. E. G.

**Estimation of the Specific Gravity of Permanent Gases at High Temperatures.** By V. MEYER and H. GOLDSCHMIDT (*Ber.*, **15**, 1161—1164).—To determine the sp. gr. of gases at a red or yellow heat, the authors employ the method lately described by them (*Ber.*, **15**, 137), but substitute for the glass bulb a straight glazed porcelain tube, 570 mm. long, and of a capacity of 100 c.c., terminating in capillary tubes, each 185 mm. long. The heating is effected by a Fletcher's tube furnace, giving with blast a temperature of about 1200°, and without the blast of about 800°. To avoid cracking the tube, the heating must be slow, some hours being taken to raise the tube to the required temperature. In making a determination, the heated tube is filled with dry air or nitrogen, this is then displaced into a measuring tube by means of a stream of the (absorbable) gas whose density is required, this is then in turn driven into a weighed absorption apparatus by a stream of dry air. The corrections are the same as in the former paper (*loc. cit.*) Determinations of the density of carbonic anhydride gave 1.55 at 802° (calculated 1.53) and 1.49 at 1180° (calculated 1.53). A series of determinations for cyanogen gave density at 100° = 1.82, at 182° = 1.83, at 250° = 1.79, at 310° = 1.76, at 446° = 1.81, and at about 800° =  $\begin{cases} 1.78 \\ 1.81 \end{cases}$  (calculated 1.80). A determination could not be made at about 1200°, the cyanogen suffering decomposition at that temperature.

A. J. G.

**Determination of Vapour-densities at the Boiling Point of Selenium.** By L. TROOST (*Compt. rend.*, **95**, 30—33).—The author employed bulbs of about 300 c.c. capacity, constructed of very infusible glass. Two determinations of the vapour-density of iodine gave the numbers 8.57 and 8.53 respectively: hence it is evident that at 665° the coefficient of expansion of iodine vapour does not differ materially from that of air, although its coefficient of compressibility is very different. Two determinations of the vapour-density of sulphur gave the numbers 2.94 and 2.92, which show that the modification of sulphur having the vapour-density 6.6, splits up gradually into that having the vapour-density 2.2, just as ozone splits up gradually into oxygen.

C. H. B.

**Experiments on the Diffusion of some Organic and Inorganic Compounds.** By J. D. R. SCHEFFER (*Ber.*, **15**, 788—801).—The

diffusion constants, as defined by Fick (*Pogg. Ann.*, **94**, 59), have been determined by a method described by Simmler and Wilde (*ibid.*, **100**, 217), which has been elaborated from Fick's formula (*loc. cit.*). The following tables contain the mean of the values obtained for the "diffusion constants" of the substances investigated:—

Substance employed.	Temperature of observation.	Diffusion constant.	Number of observations.
Hydrochloric acid .....	7·5°	2·17	6
„ .....	8	1·99	3
„ .....	8·5	2·21	4
„ .....	9	2·13	2
„ .....	15·5	2·56	2
„ .....	6·5	1·865	3
Oxalic acid.....	7·5	0·702	3
Acetic acid.....	8	0·66	3
„ .....	14·5	0·80	3
Tartaric acid .....	9	0·45	4
Succinic acid.....	15	0·546	3
Citric acid .....	9	0·41	3
Mannitol.....	10	0·58	3
Sodium acetate.....	14	0·70	4
„ .....	15	0·68	3
Chloralhydrate .....	9	0·53	4
Ammonium chloride .....	17·5	1·314	17·5

Graham's determinations give a diffusion constant for hydrochloric acid at 5° = 1·742. The author finds it to be 2·07 at 8°, and 2·57 at 15·5°. Supposing the rate of diffusion to vary according to the formula  $K_t = K_0(1 + at)$ , then from the equations  $2·07 = K_0(1 + 8a)$  and  $2·57 = K_0(1 + 15·5a)$ ; the values for  $K_0$  and  $a$  can be calculated, and the value for  $K$  at 5°; this latter was found to be 1·77, which agrees very well with Graham's result. P. P. B.

**Influence of the Compressibility of the Elements on the Compressibility of their Compounds.** By L. TROOST (*Compt. rend.*, **94**, 135—137).—The researches of V. Meyer, Crafts and Meier, and the author, have shown that the coefficient of expansion of iodine vapour increases with the temperature, and that its coefficient of compressibility diminishes with the pressure. The coefficient of compressibility of chlorine is practically the same as that of air. By determinations of vapour-density at low pressures, the author finds that the coefficients of compressibility of mercury vapour and mercuric chloride vapour at 440° are the same as that of air, whilst that of mercuric iodide vapour, at the same temperature, diminishes with the pressure. The vapour-density of the iodide vapour at 440° is 15·89 at 753·1 mm., 14·90 at 84·12 mm., and 14·82 at 46·3 m.m. It is evident therefore that the anomalous behaviour of iodine is also exhibited by its compound with mercury. C. H. B.

## Inorganic Chemistry.

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**Vapour-density of Chlorine Dioxide.** By L. PEBAL and G. SCHACHERL (*Annalen*, **213**, 113—124).—This paper contains a description of the method adopted to determine the vapour-density of this compound. The results obtained show that at temperatures about  $1^{\circ}$  above its boiling point the molecular formula of this body is  $\text{ClO}_2$ , and not  $\text{Cl}_2\text{O}_4$ . The density at  $10.7^{\circ}$  and 718.05 mm. was found to be 2.3894 (air = 1), and consequently the molecular weight is 34.50, whilst theory requires 33.64. It is not considered probable that even in the state of liquid such molecules as  $\text{Cl}_2\text{O}_4$  exist, for it is scarcely possible that they would dissociate within the limits of  $1^{\circ}$ , and the difference between the observed and theoretical densities may possibly arise from the vapour not having assumed a state to which Avogadro's law can be applied. P. P. B.

**Action of Ozone on Metallic Salts and Oxides.** By MAILFERT (*Compt. rend.*, **94**, 860—863).—*Mercurous Salts.*—The *nitrate* is entirely decomposed by ozone, with formation of mercuric nitrate and a yellow precipitate of trimercuric nitrate. The *sulphate* behaves in a similar manner, mercuric sulphate and basic sulphate being formed. Mercurous *chloride* is acted on somewhat more slowly with formation of mercuric chloride, and a brick-red precipitate, apparently an oxychloride. The *bromide* is acted on in a similar manner. With the *iodide* the action is extremely slow, mere traces of red precipitate being produced even after the ozonised gas had been passed for 15 hours.

*Silver Salts.*—With the *nitrate*, a bluish-black flocculent precipitate of peroxide is produced, which, however, is decomposed and redissolved on agitating the solution. The *sulphate* likewise gives peroxide, but the *chloride* and *cyanide* are only very slowly acted on.

*Palladium Salts.*—The *nitrate*, *chloride*, and *protoxide* give the dioxide by the action of ozone. The *protoxide*, in presence of potassium hydroxide, gives potassium palladate.

*Cobalt and Nickel Salts.*—The *sulphates*, *nitrates*, and *chlorides*, are but slowly attacked. The *protoxides*, on the other hand, are easily converted into the peroxides.

*Lead Salts.*—All the basic salts give lead peroxide, as do many of the neutral salts; the *chloride*, *nitrate*, *oxalate*, and *phosphate*, however, are but very slowly acted on. Lead oxide is also changed into peroxide by ozone, in presence of potassium hydroxide, it gives potassium plumbate.

*Manganese Salts.*—All the manganese salts, in moderately concentrated solution, give a brown or black precipitate, consisting of the hydrated dioxide if the ozone is in excess, and of a lower oxide if it is not. In the former case a violet solution, containing permanganic acid, is frequently produced. If excess of ozone acts on a very dilute solution of a manganous salt (in 30,000 to 60,000 of water), a brown dichroic solution is obtained, which slowly decomposes after a time,



depositing a rusty brown precipitate, and leaving permanganic acid in solution.

*Chromic Salts*.—The sulphate, chloride, and oxide all yield chromic acid. If ether is present, perchromic acid is formed.

*Bismuth oxide* gives bismuthic acid, and in presence of potassium hydroxide potassium bismuthate.

*Iron sesquioxide* is not acted on by ozone, but in presence of potassium hydroxide it yields potassium ferrate. C. E. G.

**New Compounds of Ammonia with Nitric and Acetic Acid.** By L. TROOST (*Compt. rend.*, **94**, 789—792; *Comp. Abstr.*, 1881, 972).—*Combinations of Nitric Acid with Ammonia*.—Divers observed that ammonium nitrate was capable of absorbing a large amount of dry gaseous ammonia, forming a compound varying in composition with the temperature and pressure at which the experiment was made. By observing, however, the tension of the gas emitted by this compound, as in the case of the compound of the halogen hydrides with ammonia (*loc. cit.*), the author has established the existence of a compound  $2(\text{NH}_4.\text{NO}_3) + 3\text{NH}_3$ . It is solid at a low temperature, and melts to a mobile liquid at  $-22^\circ$ , the tension of dissociation at  $-30^\circ$  is 90 mm. Indications of the existence of a compound  $\text{NH}_4.\text{NO}_3 + 3\text{NH}_3$  were also obtained.

*Combinations of Acetic Acid with Ammonia*.—Two compounds of ammonia with acetic acid have been obtained of the formulæ  $\text{NH}_4.\text{OAc} + 3\text{NH}_3$  and  $\text{NH}_4.\text{OAc} + 6\text{NH}_3$ , both crystallise in thin rhomboidal plates, but the first melts at  $-18^\circ$ , and the second at  $-32^\circ$ . Their tension of dissociation, taken above their fusion points, is constant for the same temperature, and increases rapidly as the temperature rises. C. E. G.

**Behaviour of Nitrogen Peroxide in the Manufacture of Sulphuric Acid.** By G. LUNGE (*Dingl. polyt. J.*, **244**, 247—248).—Contrary to the opinion held by Benker and Lasne that all compounds of oxygen and nitrogen are contained in the chamber exit gases as nitrogen peroxide, which combines only loosely with sulphuric acid, Lunge shows that nitrogen peroxide is readily and completely absorbed by sulphuric acid of  $60^\circ \text{B}$ . The colourless solution obtained neither alters on continued heating at  $100^\circ$ , nor changes when air is drawn through it for some time: hence it does not contain unaltered or loosely combined nitrogen tetroxide, but behaves like a mixture of sulphuric acid, nitrosyl sulphate, and nitric acid. Benker and Lasne's theory is therefore erroneous. Their process is novel only inasmuch as sulphurous acid and steam are worked in a special apparatus; it however requires great care in manipulating, as an excess of steam and sulphurous acid has a denitrating action on the nitrosyl sulphate produced, and results in the formation of the bluish-violet solution of the unstable compound, intermediate between NO and  $\text{N}_2\text{O}_3$ , nitric oxide escaping simultaneously. The behaviour of nitrogen peroxide with sulphuric acid, as above shown, is a further proof of the existence of the molecule  $\text{N}_2\text{O}_3$  in the gaseous state. (See *ibid.*, **233**, 63, and *Abstr.*, 1880, 440.) D. B.

**Hydrates formed under Pressure and by Sudden Expansion.** By L. CAILLETET and BORDET (*Compt. rend.*, **95**, 58–61).—When phosphuretted hydrogen is compressed in presence of water in the apparatus employed for the liquefaction of gases, the gas liquefies and floats on the surface of the water, in which it partly dissolves. If the pressure is suddenly released, a white crystalline body is formed in the tube, but if the pressure is reduced below a certain point the compound dissociates. The formation and dissociation of this compound, which is undoubtedly phosphonium hydroxide, although it has not yet been analysed, take place at perfectly definite pressures for a given temperature. Above  $+28^{\circ}$ , the compound does not form under any pressure. By carefully heating the tube, the crystalline deposit can be distilled from one part of the tube to another, and condenses in very distinct crystals. On compressing equal volumes of phosphuretted hydrogen and carbonic anhydride in presence of water, a white crystalline body is formed without any gaseous residue. It is a mixture of phosphonium hydroxide with the hydrated carbonic acid discovered by Wroblewski (this vol., p. 1026), and is not formed above  $+22^{\circ}$ . On compressing a mixture of dry phosphuretted hydrogen and carbon bisulphide, no compound is formed, but in presence of a little water a solid white crystalline substance is deposited: this dissociates on raising the temperature or lowering the pressure. Under the same conditions, hydrogen sulphide combines with water (comp. this vol., p. 1027, and *Compt. rend.*, **95**, 129), but the hydrate is not formed above  $+29^{\circ}$ , a temperature almost the same as in the case of the phosphonium hydroxide. With ammonia gas and water, no solid body is obtained, but if the tube contains air, thick white vapours of ammonium hydroxide are formed when the pressure is suddenly reduced.

C. H. B.

**Purification of Sulphuric Acid by Crystallisation.** By R. S. TJADEN-MODDERMANN (*Zeits. Anal. Chem.*, **21**, 218).—G. Lunge's observation as to the ease with which sulphuric acid crystallises by cooling is confirmed, and the purification of the acid in this way for analytical use is recommended.

O. H.

**Hydration of Salts.** By HAMMERL (*Monats. Chem.*, **3**, 419–427).—The author remarks that our knowledge of hydrated salts is still very defective. Many salts indeed are known to form a considerable number of hydrates, and the conditions under which these several hydrates are formed are in many cases accurately defined; but we are not in a position to say, with regard to any single salt, that we are acquainted with all its possible hydrates, inasmuch as we have no certain method of obtaining them all. J. Thomsen's method (*J. pr. Chem.* [2], **18**, 1) of pulverising the salts in their highest state of hydration, and drying them down to the calculated water-amount of the desired hydrate is unsatisfactory, inasmuch as it gives no assurance that a definite hydrate is obtained, and not a mixture of several.

To obtain more exact results, the author has endeavoured to conduct the crystallisation of a salt in such a manner that the formation of successive hydrates shall depend upon the temperature alone, so that

there may be a certainty of obtaining all the hydrates that are possible between two limits of temperature, by causing the crystallisation to take place gradually at all intermediate temperatures. To ensure this, the unsaturated solution of a salt must be brought to a series of constant temperatures, and the crystallisation must be effected, not by cooling, but by gradual removal of the solvent, care being taken to avoid local cooling, which might take place if the solvent were removed merely by surface evaporation. This result may be attained in two ways—(1.) By passing through a solution of the salt not quite saturated at a given temperature a stream of dry air, which on the one hand keeps it in a state of agitation, and on the other effects a gradual removal of water-molecules, thereby giving rise to the crystallisation of a hydrate. To prevent supersaturation, crystals having the expected composition are thrown into the liquid from time to time. (2.) By bringing a solution saturated at a given temperature and the corresponding pressure, to the boiling point, and removing the resulting water-vapour by condensation.

Of these methods—for the details of which the original paper must be consulted—the latter was found to give the more exact results, and a series of experiments made by it on sodium carbonate,  $\text{Na}_2\text{CO}_3$ , which is known to form hydrates containing 1, 3, 5, 6, 7, and 10 molecules of water, led to the following conclusions:—Between  $15^\circ$  and  $95^\circ$  C. only two hydrates, viz., those with 1 and 10 mols. water, can be obtained with certainty, by evaporation of the water; and the temperature  $34^\circ$ , at which the 10-hydrate melts in its crystal-water, forms the limit between the two, the monohydrate being produced above, and the decahydrate below it. Of the other known hydrates, those containing 3, 5, 6, and 7 mols. water (the last in two modifications) cannot be prepared by the method in question, inasmuch as their formation appears to depend, not solely upon temperature, but also upon certain accidental conditions, especially on the non-formation of the decahydrate in consequence of supersaturation. The existence of the other hydrates appears, therefore, to depend upon a condition of unstable equilibrium, inasmuch as they cannot be formed simultaneously with the decahydrate.

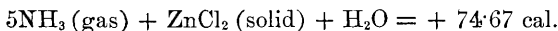
The general conditions which determine the formation of a hydrated salt appear, therefore, to be as follows:—When a saline solution is gradually concentrated, or its temperature lowered, then, after a certain degree of concentration, the point of saturation for a particular hydrate is passed over, *i.e.*, the solution, with respect to that hydrate, becomes supersaturated; but whether crystallisation takes place or not depends on accidental circumstances. On further concentration, the solution gradually becomes supersaturated for another, and ultimately for several hydrates. All the hydrates for which this supersaturation exists are therefore possible, that is to say, they may crystallise out under certain circumstances. But amongst them there exists a series of probability of formation, and only one of them, viz., the most stable, can be obtained with certainty. The determination of the saturation-points of the several possible hydrates is, however, difficult, and presupposes the possession of ready-formed crystals.

H. W.

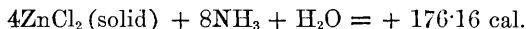
**Remarks on Didymium.** By P. T. CLÈVE (*Compt. rend.*, **95**, 33).—The line 4333·5, which the author regarded as belonging to a new element, occupying a position between lanthanum and didymium, is in reality one of the lines of lanthanum, although not given in Thalén's list. The line 4330 given by Thalén does not exist in the spectrum of lanthanum. Experiments made by Thalén and the author indicate that the existence of a new element between lanthanum and didymium is improbable.

C. H. B.

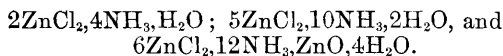
**Ammoniacal Zinc Chlorides.** By G. ANDRÉ (*Compt. rend.*, **94**, 963—966).—If gaseous ammonia is passed into a solution of zinc chloride in cold concentrated ammonia, and the mixture is then heated until the crystalline precipitate is redissolved, the solution on cooling deposits large octohedral crystals, to which Divers assigned the formula  $5\text{NH}_3\cdot\text{ZnCl}_2\cdot\text{H}_2\text{O}$ . This compound dissolves easily in a small quantity of water, but is decomposed on diluting the solution. Its heat of formation is—



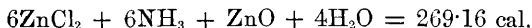
Kane's compound,  $4\text{ZnCl}_2\cdot 8\text{NH}_3\cdot\text{H}_2\text{O}$ , prepared by passing ammonia into a hot concentrated solution of zinc chloride until the precipitate is redissolved, gave the following results:—



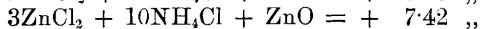
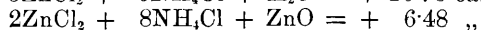
Other compounds obtained by the action of ammonia on zinc chloride under varying circumstances, have the composition—



The heat of formation of the last-mentioned is—



Compounds of zinc chloride, ammonium chloride, and zinc oxide were also prepared, and their heats of formation determined as follows:—



The first compound crystallises in large plates very soluble in water: the other two are also crystalline, but are decomposed by water.

The author is studying the oxychlorides of zinc.

C. E. G.

**Cuprous Sulphites and their Derivatives.** By ETARD (*Compt. rend.*, **95**, 36—38 and 137—140).—In a previous note the author has shown that the action of sulphurous anhydride on a solution of cupric acetate yields at first the salt  $\text{S}_8\text{O}_3\cdot\text{Cu}'_2\text{Cu}''_{10}\text{H}_{10} + 21\text{H}_2\text{O}$ , described by P. de Saint-Gilles. If a current of sulphurous anhydride is passed into a solution of cupric acetate at  $85^\circ$ , a granular, yellow precipitate,

of the composition  $\text{S}_8\text{O}_{32}\text{Cu}'_4\text{Cu}''_{14}, \text{Cu}_2\text{O} + 5\text{H}_2\text{O}$ , is formed, and by further action of the gas this is converted into the compound  $\text{SO}_3\text{Cu}_2, \text{SO}_3\text{Cu} + 2\text{H}_2\text{O}$ , described by Chevreul. By varying the temperature and relative proportions of acid and water, a whole series of basic salts can be obtained with colours varying from light-brown to deep violet. If the solution is very dilute, cuprous oxide is formed. All these basic salts are perfectly homogeneous and crystallise well, but the proportion of copper varies as if their composition was governed by the physical conditions and not by the laws of chemical combination. One of these salts was obtained several times in violet crystals of the composition  $\text{SO}_3\text{Cu}_2, 9\text{Cu}_2\text{O}$ .

When crystallised basic cupric acetate is dissolved in acetic acid of  $8^\circ$ , and sulphurous anhydride is passed into the boiling saturated solution, the latter acquires a deep blue colour, and a heavy precipitate of white nacreous plates is formed. The passage of the gas is discontinued before this precipitate is converted into the violet compounds previously mentioned, the liquid is decanted off, and the precipitate washed on a filter with water, alcohol, and ether. This new salt is *cuprous sulphite*,  $\text{SO}_3\text{Cu}_2 + \text{H}_2\text{O}$ , which has not previously been isolated with certainty. It forms colourless or slightly amber hexagonal tables which act on polarised light; sp. gr. at  $15^\circ = 3.83$ .

Tagosky stated (*Compt. rend.*, 1851) that red cuprous sulphite is obtained by treating cuprous ammonium sulphite,  $\text{SO}_3\text{Cu}_2, \text{SO}_3(\text{NH}_4)_2 + 2\text{H}_2\text{O}$ , with sulphurous acid, but Saint-Gilles was unable to obtain this compound. The author finds that by prolonged and repeated digestion with sulphurous acid, the cuproso-ammonium salt, which forms colourless hexagonal crystals, is completely converted into brick-red prismatic crystals which act on polarised light and have the empirical composition  $\text{SO}_3\text{Cu}_2 + \text{H}_2\text{O}$ ; sp. gr. at  $15^\circ = 4.46$ . This compound is more readily obtained by the action of sulphurous acid on the sodium salt  $\text{SO}_3\text{Cu}_2, \text{SO}_3\text{Na}_2 + 2\text{H}_2\text{O}$ , thus,  $\text{SO}_3\text{Cu}_2, \text{SO}_3\text{Na}_2, 2\text{H}_2\text{O} + \text{SO}_3\text{H}_2 = \text{SO}_3\text{Cu}_2, \text{H}_2\text{O} + \text{H}_2\text{O} + 2\text{SO}_3\text{NaH}$ . Cuprous sulphite exists, therefore, in two isomeric modifications which differ in colour and specific gravity. The white modification may be converted into the red by prolonged digestion with sulphurous acid in sealed tubes. The white salt corresponds with the white cuprous chloride and acetate, and is the normal cuprous sulphite. The red salt, *cuprous isosulphite*, is in all probability a polymeride, a supposition which is confirmed by the composition of a derivative mentioned hereafter. With the exception of the fluo-salts this is the only known instance of isomerism amongst true inorganic salts.

Normal cuprous sulphite combines readily with sodium hydrogen sulphite to form the white crystalline salt  $\text{SO}_3\text{Cu}', \text{SO}_3\text{Na}_2 + \text{H}_2\text{O}$ , insoluble in water, but slowly decomposed by a large excess of the latter. This salt has previously been obtained by Commaille and Svensson under very different conditions. By treating different copper solutions with sulphites, Saint-Gilles, Commaille, and Svensson have obtained a number of double salts of the general formula  $\text{SO}_3\text{Cu}_2, \text{SO}_3\text{M}_2 + 2\text{H}_2\text{O}$ . The author has obtained the sodium, potassium, and ammonium salts described by those chemists, and also the lithium salt, by boiling Chevreul's salt with the corresponding alkaline

hydrogen sulphites. The alkali-metals displace the copper, which passes into the cuprous condition and forms a new double salt, whilst sulphurous anhydride is given off, thus:  $2(\text{SO}_3\text{Cu}_2, \text{SO}_3\text{Cu} + 2\text{H}_2\text{O}) + 6\text{SO}_3\text{NaH} = 3(\text{SO}_3\text{Cu}_2, \text{SO}_3\text{Na}_2 + 2\text{H}_2\text{O}) + \text{SO}_4\text{H}_2 + 3\text{SO}_2$ . An intimate relation exists between the cuproso-sodium salts and Chevreul's salt. They all contain cuprous copper as an essential constituent, and the other metals,  $\text{K}_2$ ,  $\text{Na}_2$ ,  $\text{Li}_2$ ,  $(\text{NH}_4)_2$ ,  $\text{Cu}''$ , can undergo reciprocal displacement without in any way altering the type of the resulting salt. The same changes would take place if there existed an acid sulphite,  $\text{SO}_3\text{Cu}_2, \text{SO}_3\text{H}_2 + 2\text{H}_2\text{O}$ , but the author has shown that although the cuproso-alkaline salts lose their alkaline metal when treated with sulphurous acid, a normal and not an acid sulphite is formed, hence it would appear that the acid salt is not stable in the free state, but loses its acid and becomes polymerised, forming cuprous isosulphite.

The salt  $\text{SO}_3\text{Cu}_2, \text{SO}_3\text{Na}_2 + 11\text{H}_2\text{O}$ , derived from normal cuprous sulphite, is connected with Chevreul's salt and the ordinary cuproso-alkaline sulphites. It may in fact be regarded as a more highly hydrated form of the salt  $\text{SO}_3\text{Cu}_2, \text{SO}_3\text{Na}_2 + 2\text{H}_2\text{O}$ . On the other hand, Chevreul's salt may be obtained from the normal sulphite by first converting it into the double sodium salt.

Cuprous isosulphite, when gently heated with a concentrated solution of sodium hydrogen sulphite, yields a chamois-coloured compound of the composition  $\text{S}_8\text{O}_{32}(\text{Cu}_2)_3\text{Na}_{16}\text{H}_{10} + 43\text{H}_2\text{O}$ . This salt belongs to the series of octo-sulphites, several of which the author has previously described, and its formation indicates that the formula of the isosulphite is  $\text{S}_8\text{O}_{32}(\text{Cu}_2)_8\text{H}_{16} = (\text{SO}_3\text{Cu}_2, \text{H}_2\text{O})_8$ .  
C. H. B.

**Decomposition of Gallium Protochloride by Water.** By L. DE BOISBAUDRAN (*Compt. rend.*, **95**, 18).—The author has already observed that when anhydrous gallium protochloride is dissolved in water, gas is evolved in quantity which increases with the degree of dilution. A precisely similar effect is produced when metallic gallium is dissolved in the cold in a small quantity of concentrated hydrochloric acid. The limpid liquid thus obtained gives off gas only very slowly, but if diluted with water a rapid evolution of gas takes place. Each fresh dilution causes renewed evolution of gas, but the total volume given off is about 10 c.c. for every 0.1 gram of metal. We have here an example of a metallic protochloride sufficiently stable to be formed in presence of water, but rapidly passing into perchloride, with evolution of hydrogen, as the quantity of water present is increased.  
C. H. B.

**Chromammonium-compounds.** By S. M. JÖRGENSEN (*J. pr. Chem.* [2], **25**, 321—348).—In this paper, the intermediate products of the oxidation of chromammonium chloride into chloropurpureochromium salts are investigated, thus furnishing an explanation of the oxidation process.

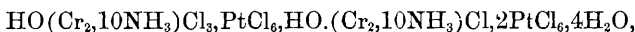
When air is passed through the dark blue ammoniacal solution of chromium bromide, a blue crystalline salt separates, which, by dilute

hydrobromic acid, is converted into a beautiful salt, quite different from bromopurpureochromium bromide, and called by the author *rhodochromium bromide*. Rhodochromium chloride is likewise produced during the preparation of chloropurpureochromium chloride (this Journal, 38, 10), and separates out in rose to carmine-red prisms, as soon as the blue ammoniacal solution comes in contact with the air. Rhodochromium salts dissolve in ammonia or soda with a blue colour, and are precipitated as blue crystalline *basic salts* by alcohol or neutral salt solutions; acids reconvert these into the normal salts. The blue solution of the rhodo-salts very soon undergoes a change, with formation of a new series of red salts, isomeric with the rhodo-salts. The author calls these *erythrochromium salts*. They are precipitated from the solution by acids, are soluble in ammonia with a carmine colour, and are precipitated as carmine, crystalline, *basic salts*, which are in their turn reconverted into normal salts in the same way as the rhodo-salts. Boiling with concentrated hydrobromic acid converts the bromides of all the four series into bromopurpureochromium bromide.

Normal Rhodochromium Salts.—*Rhodochromium bromide*,  $\text{HO}(\text{Cr}_2, 10\text{NH}_3)\text{Br}_3, \text{H}_2\text{O}$ , can be prepared in three ways. 1.—Ten grams of chromium oxide, in the form of hydrate, are dissolved in 100 c.c. of concentrated hydrobromic acid, the green solution is poured on the zinc in a Christensen's apparatus, and 30 c.c. of half-dilute hydrobromic acid are added. As soon as the liquid is quite blue (after about 10 minutes), the evolution of hydrogen is quickened by the further addition (30 c.c.) of the half-dilute acid, the liquid being forced over by the pressure into a solution of 150 grams of ammonium bromide in 750 c.c. of strong ammonia. The deep-blue solution thus produced, after removing any zinc, is oxidised by means of a stream of air. The liquid is decanted as quickly as possible from the blue crystalline precipitate of basic rhodochromium bromide thus formed, which is then treated with excess of diluted hydrobromic acid (1 vol. acid to 3 vols. water), whereby it is changed into the red normal salt. 2.—One gram of rhodochromium chloride is dissolved in about 60 c.c. of cold water (not in sunlight), filtered, and mixed with 10 c.c. concentrated hydrobromic acid: almost all the chromium separates out as rhodobromide. 3.—Erythrochromium bromide is converted into the rhodo-salt by heating for 24 hours at  $100^\circ$ . When pure, rhodochromium bromide forms a rather bulky pale carmine-red crystalline (needles) powder. The air-dried salt loses 1 mol.  $\text{H}_2\text{O}$  by exposure over sulphuric acid for 10 to 15 days. When heated in the air, it is resolved far below red heat into chromium oxide. It is only slightly soluble in cold water, with a violet-red colour and neutral reaction. When warmed, the solution becomes blue-violet, and boiling either alone or with soda entirely decomposes it, ammonia being given off and chromium hydroxide deposited. This change takes place gradually even in the dark. The salt is insoluble in dilute hydrobromic acid and in aqueous ammonium bromide. If it is boiled with water containing a small quantity of hydrobromic acid, it is converted into roseochromium bromide; on the other hand, with the concentrated acid, it yields bromopurpuro-bromide; this reaction is nearly quantitative. It is

therefore evident that the rhodo-salt contains 10 mols.  $\text{NH}_3$  to 2 atoms chromium. With silver nitrate, all the bromine is precipitated, and, when shaken with freshly precipitated silver chloride and filtered, the filtrate contains the rhodochloride. By dilute soda or ammonia, however, one bromine-atom only is removed, and the blue basic rhodobromide remains in solution; if sodium thiosulphate is at once added to this blue solution, *basic rhododithionate* separates out as a blue crystalline precipitate of glittering leaflets. Alcoholic ammonia precipitates blue basic rhodobromide from the rhodobromide solution. With dilute hydrochloric acid (1 to 2), the cold freshly prepared saturated rhodobromide solution gives a violet-red precipitate of impure rhodochromium chloride. Hydrobromic, hydriodic, dilute nitric, and dilute sulphuric acids (especially in presence of alcohol) behave in a similar manner, the respective rhodochromium salts being precipitated. Platinum bromide gives a scarlet-red precipitate of microscopic four-rayed stars. Its behaviour with various reagents is also described. *Rhodochromium chloride* can be prepared from the bromide by filtering the solution into half-dilute hydrochloric acid; it is purified in a manner similar to the bromide. Or thus, chromium chloride solution from 60 grams potassium dichromate is reduced by Christensen's method (*J. pr. Chem.* [2], 23, 56), and then driven into 500 grams ammonium chloride dissolved in 750 c.c. strong ammonia; the blue solution is then very quickly oxidised by shaking with free oxygen; it turns red, and rhodochromium chloride separates. In the pure state, rhodochromium chloride forms a bulky pale carmine mass of thin small needles. It loses 1 mol.  $\text{H}_2\text{O}$  over sulphuric acid. Heated for several days at  $130^\circ$ , it becomes grey-green; at higher temperatures it behaves like the bromide. With most reagents, it behaves in a manner similar to the bromide. Aqueous ammonia saturated with ammonium chloride has no action on it. Heated just to boiling with dilute ammonia (1 gram with 10 c.c.), and then quickly cooled and treated with 3 vols. concentrated hydrobromic acid, yellow roseochromium bromide is formed. With silver carbonate, *rhodochromium carbonate* is produced, forming a blue-violet solution with alkaline reaction; from this solution, sodium thiosulphate precipitates rhododithionate, and alcohol an oil which dissolves in water and gives with dilute nitric acid a precipitate of rhodochromium nitrate with evolution of carbonic anhydride. With freshly precipitated silver oxide and water, rhodochromium chloride gives rise to blue *rhodochromium hydroxide*, which very quickly changes into the carmine-red *erythrorhodium hydroxide*; this in its turn is very quickly oxidised to *roseochromium chromate*, with separation of metallic silver. Many additional reactions of the rhodochromium chloride are also given.

*Rhodochromium aurochloride*,  $\text{HO}(\text{Cr}_2, 10\text{NH}_3)\text{Cl}_3, 2\text{AuCl}_4, 2\text{H}_2\text{O}$ , forms reddish-yellow needles, soluble in cold water; they give up the 2 mols.  $\text{H}_2\text{O}$  at  $100^\circ$ ; when heated over a flame, they decompose suddenly with crackling noise. The *platinochloride*,



is an orange-red crystalline precipitate. *Rhodochromium iodide* is prepared and purified in a manner analogous to the bromine and chloride.



It is a pale violet-red precipitate, with silky lustre, consisting of very small prisms; it loses 1 mol.  $\text{H}_2\text{O}$  at  $100^\circ$ . Its other properties are similar to those of the chloride and bromide. *Basic rhodochromium iodide* forms brilliant indigo-blue crystals (octohedra). *Rhodochromium nitrate*,  $\text{HO}(\text{Cr}_2, 10\text{NH}_3)_2, 5\text{NO}_3$ , prepared by filtering a solution of the chloride or bromide into cold dilute nitric acid, and purifying as usual, forms a rose or carmine mass of microscopic needles, frequently in fern-like aggregations. At  $100^\circ$  it gradually decomposes with considerable loss of weight, becoming blue-green. When heated in the air, it takes fire below a red heat and swells up to an extraordinarily porous, glistening, greenish-grey chromium oxide. Rhodochromium nitrate dissolves in water, forming a red solution: it is, however, only very slightly soluble in dilute nitric acid, and when boiled therewith, is partially converted into the roseonitrate; if too little nitric acid is used, the liquid becomes deep violet-red, and, on cooling, sets to a bluish-grey jelly of ammoniacal chromium hydroxide. Boiling with concentrated nitric acid converts the salt completely into chromium and ammonium nitrates, thus showing that the nitropurpuro-salts of the chromium series are not stable, differing in this respect from those of the cobalt series. Boiling with ammonia changes the colour without the formation of erythronitrate. Gold chloride and mercury chloride give no precipitate until dilute hydrochloric acid has been added to the solution of the rhodonitrate. Platinum chloride gives the same precipitate under all circumstances, viz., long red-yellow microscopic needles with cleft edges, sometimes in cruciform groups, with acute or more frequently right angles. Other reactions are the same as those of the bromide and chloride. *Rhodochromium sulphate* is prepared by adding dilute sulphuric acid to a cold aqueous solution of the chloride. The salt is washed with a mixture of water (3 vols.), alcohol (1 vol.), and dilute sulphuric acid; it forms carmine-coloured tables. When heated at  $100^\circ$ , it decomposes, loses weight, and becomes violet. It is almost insoluble in water; the solution, however, is coloured blue by ammonia. It dissolves readily in cold dilute sulphuric acid, with a splendid carmine colour; this solution, when dilute, gives a precipitate with dilute nitric acid. Concentrated ammonia is apparently almost without action on the sulphate, but dilute soda dissolves it with a blue colour, and shows the thiosulphate reaction. Platinum chloride gives a bulky, pale-red precipitate of slender needles. When boiled, the sulphuric acid solution of the sulphate undergoes no visible change. *Rhodochromium dithionate*,  $(\text{HO}.\text{Cr}_2, 10\text{NH}_3)_2, 5\text{S}_2\text{O}_6, 2\text{H}_2\text{O}$ , is precipitated on adding sodium thiosulphite to the solution of the chloride in very small pale-red crystals, which become darker after washing with water, and consist of carmine-red rhombic prisms. The salt loses all its water over sulphuric acid. At  $100^\circ$  it becomes violet, and gradually decomposes.

*Basic Rhodochromium Salts.*—*Basic rhodochromium bromide*,  $\text{HO}(\text{Cr}_2, 10\text{NH}_3).\text{OH}.\text{Br}.\text{H}_2\text{O}$ , the blue crystalline precipitate obtained in process 1 (see above) for the preparation of rhodochromium bromide, is washed with a mixture of ammonia and alcohol, then with alcohol alone, and dried in the air. This salt is a moderately dark-blue coarse crystalline powder of microscopic octohedrons, frequently

united in four-rayed stars. It loses 1 mol.  $\text{H}_2\text{O}$  on exposure over sulphuric acid for 48 hours, and after a long time (several months), decomposes, losing ammonia, and becoming lilac-coloured; the same change takes place when the substance is left in closed vessels in the dark. At  $100^\circ$ , it loses weight and becomes greenish. Dilute hydrobromic acid and also ammonium bromide convert it into the normal bromide, but strongly ammoniacal solutions of ammonium bromide do not alter it: hence the necessity of having plenty of ammonia present during its preparation. The dry salt is slightly soluble in water, with a faint alkaline reaction and blue colour, which very soon changes to red, owing to the formation of basic erythrochromium bromide. It is insoluble in alcohol. *Basic rhodochromium chloriodide*,  $\text{OH}(\text{Cr}_2, 10\text{NH}_3) \cdot \text{OH}, \text{Cl}_2\text{I}_2$ , is precipitated in coarse dark-blue granules of pointed pyramids when 6 grams of ammonium iodide dissolved in 50 c.c. of water are added to 2 grams of rhodochromium chloride dissolved in 50 c.c. of cold dilute ammonia. It is washed in the same way as the above basic salt, which it resembles in properties. *Basic rhodochromium dithionate*,  $\text{OH}(\text{Cr}_2, 10\text{NH}_3) \cdot \text{OH}, 2\text{S}_2\text{O}_6, \text{H}_2\text{O}$ , is the pale blue precipitate formed when sodium thiosulphate is added to a soda or ammonia solution of a normal rhodochromium salt; it is washed with water, then with alcohol, and dried in the air. It is insoluble in water and dilute ammonia or soda. The pure dry salt undergoes decomposition, even in closed vessels, and in the dark, ammonia is evolved and a tetramine salt is formed, recognised by its solubility in concentrated hydrochloric acid, and by the formation of rhombic tables of a chlorotetramine sulphate when shaken with aqueous ammonium sulphate.

D. A. L.

**Molybdenum Fluorides.** By F. MAURO and R. PANEBIANCO (*Gazzetta*, 12, 180—182).—In order to establish the relation between molybdenum and the niobium group (vanadium, niobium, and tantalum), the titanium group (zirconium, titanium, and tin), and chromium, the author has undertaken the investigation of molybdenum compounds of the formula  $\text{MoX}_5$ ,  $\text{MoX}_4$ ,  $\text{MoX}_3$ ,  $\text{MoX}_2$ , and particularly of the molybdenum double fluorides.

When hydrated molybdenum dioxide is dissolved in a concentrated boiling solution of potassium fluoride, and allowed to cool, it deposits the compound  $\text{MoOF}_3 \cdot 2\text{KF}, \text{H}_2\text{O}$ , in very thin green laminae, which are iridescent in mass. The crystals are trimetric, and closely resemble the corresponding niobium, tungsten, and titanium compounds. It dissolves in water, with red-brown colour, and gives a blue solution with acids. It reduces potassium permanganate and ammoniacal silver solution. Ammonia precipitates molybdenum dioxide, and ammonium molybdate remains in solution. When this double fluoride is dissolved in hot hydrofluoric acid, slender, sky-blue, lustrous crystals are obtained. The solution from which the green laminae have been deposited is of a purple colour, and when left at rest for some time yields violet scales, resembling chrome-alum in colour. They give a precipitate with ammonia.

When hydrated molybdenum dioxide is dissolved in a warm dilute solution of potassium fluoride, a reddish-brown solution is obtained,

which on cooling deposits a reddish crystalline powder; this has not as yet been further examined; it probably belongs to the form  $\text{MoX}_{4,n}\text{A}$ . With the dioxide and a concentrated boiling solution of ammonium fluoride, splendid red-brown crystals are obtained, the composition of which must also be referred to the form  $\text{MoX}_{4,n}\text{A}$ . Dissolved in hydrofluoric acid, they yield green-blue crystals, resembling the potassium salt first described, and also blue needles.

The author is continuing the investigation of these compounds.

C. E. G.

**Action of Hydrogen Sulphide on Nickel Chloride.** By H. BAUBIGNY (*Compt. rend.*, **95**, 34—36; see also this vol., 805).—Under precisely similar conditions, in both neutral and acid solutions, nickel sulphate is converted into the sulphide by the action of hydrogen sulphide more easily than the corresponding chloride, and the laws which the author has previously deduced respecting the action of hydrogen sulphide on nickel sulphate hold equally well in the case of the chloride. The precipitation of nickel salts by hydrogen sulphide depends on the ratio between the weight of acid and metal present, on the nature of the acid, the temperature, the time, the tension of the hydrogen sulphide in the solution, and when heated, on the relative volumes of liquid and gas in the closed space. Nickel can be completely precipitated by hydrogen sulphide from a solution of the acetate containing free acetic acid, if the solution is heated to  $70^\circ$  and allowed to cool out of contact with air. Any oxidising agents, such as nitrates, must be decomposed by boiling with ammonium sulphide.

C. H. B.

**Basic Salts of Manganese.** By A. GORGEU (*Compt. rend.*, **95**, 82—84).—The basic manganese sulphate previously described (this vol., 1032) forms double compounds with the alkaline sulphates of the general formula  $(3\text{MnO}_2, 2\text{SO}_3 + 3\text{H}_2\text{O}) + \text{M}_2\text{SO}_4$ . The sodium salt contains an additional 2 mols.  $\text{H}_2\text{O}$ . The potassium salt forms microscopic rhombic prisms, with an angle of  $106^\circ$ , and the crystals of the ammonium salt are similar, but with a slightly different angle. The sodium salt appears to belong to the same system, but the crystals are too small to admit of measurement. The potassium and sodium compounds are obtained by adding an alkali to a boiling solution of manganese sulphate and the alkaline sulphate, until a permanent precipitate just forms, then filtering, and allowing the filtrate to cool. To prepare the ammonium salt, the solution of mixed sulphates is heated to  $80^\circ$ , and ammonia added drop by drop until crystals form. All three salts are decomposed by water, which dissolves out the alkaline sulphate, and then gradually decomposes the basic manganese sulphate, leaving a residue of monoxide, which in presence of air is gradually converted into  $\text{Mn}_2\text{O}_3$ . They are all soluble in hydrochloric acid, giving a colourless solution if recently prepared. When heated, the ammonium salt begins to lose its water at  $180^\circ$ , and at a dull red heat it leaves a residue composed entirely of normal manganese sulphate, the manganese monoxide having replaced the ammonium. Under similar conditions, the potassium and sodium salts begin to lose water at  $220^\circ$  and  $130^\circ$  respectively, and after ignition leave a residue

containing 2 mols. normal manganese sulphate, and 1 mol. alkaline sulphate, the manganese protoxide having been oxidised to sesquioxide.

C. H. B.

**Rhdammonium Compounds.** By S. M. JÖRGENSEN (*J. pr. Chem.* [2], **25**, 346—348).—The author has prepared and cursorily examined some of the rhdammonium compounds, and has found them to be strictly analogous to the cobalt- and chrom-ammonium compounds. A chloropurpureochloride,  $\text{Cl}_2(\text{Rh}_2, 10\text{NH}_3)\text{Cl}_4$ , and a chloropurpureonitrate,  $\text{Cl}_2(\text{Rh}_2, 10\text{NH}_3)4\text{NO}_3$ , have been prepared, together with the corresponding iodo-, bromo- and nitro-purpureorhodium salts; also roseo- and xantho-rhodium salts. All these salts resemble the corresponding chromium and cobalt salts in every particular except colour: with the exception of the bromopurpureorhodium salts, which are sulphur-yellow, and the iodopurpureorhodium salts, which are chrome-yellow, all the above-mentioned rhdammonium salts are white or slightly yellow.

D. A. L.

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## Mineralogical Chemistry.

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**Mechanical Separation of Minerals.** By C. DOELTER (*Monatsh. Chem.*, **3**, 411—418).—The method in use for the mechanical separation of the constituents of rocks are three in number, depending—1. On difference of density. 2. On the use of an electromagnet. 3. On the use of acids, especially hydrofluoric acid. The first, introduced by Fouqué, which consists in suspending the pulverised rock-constituents in a solution of considerable density, is perhaps the most exact, but it is not always applicable. Of the solutions used for the purpose the author regards that of mercuric iodide, recommended by Goldschmidt, as capable of affording the best results, the denser solution of cadmium-borotungstate being required in comparatively few cases.

The second method, likewise introduced by Fouqué, has been adopted and somewhat modified by the author (p. 656 of this volume), whose mode of proceeding has lately been criticised by Pebal (p. 810), who recommends that the powder to be acted upon by the electromagnet be suspended in water, instead of being used in the dry state. To this Doelter objects, on the ground that when the fine powder is suspended in water, the particles are apt to agglomerate, so that the non-ferruginous minerals are carried forward, together with ferruginous magnetic particles; further, that the loss of material is greater when water is used, and that the fine pulverisation required in this case interferes greatly with the microscopic examination, which is so highly important for the verification of the result. With regard to this electromagnetic method, the author further remarks that it is most easily performed on rocks of granular structure, the grey powder of syenites and diabases, for example, being thereby separated in a few minutes into a white powder containing the non-felspathic minerals,



**Columbite, Orthite, and Monazite, from Amelia Co., Virginia.** By F. P. DUNNINGTON (*Amer. Chem. J.*, **4**, 158—160).—Among the minerals found together with microlite, in this locality (1881, Abstr., 1002), was a variety of *columbite* having a decided red colour in thin splinters. Hardness = 5·5; sp. gr. = 6·48. Lustre subresinous. Colour dark brown. Streak light brown. It gave by analysis—

Ta <sub>2</sub> O <sub>5</sub> , Nb <sub>2</sub> O <sub>5</sub> .	SnO <sub>2</sub> .	MnO.	FeO.	CaO.	MgO.	Y <sub>2</sub> O <sub>3</sub> ?
84·81	trace	8·05	5·07	1·27	0·20	0·82 = 100·22

The excess of manganese over iron probably accounts for the unusual red colour of the splinters, and the light colour of the streak.

The density of the mixed acid oxides is 6·51. Now pure Ta<sub>2</sub>O<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub>, similarly ignited, gave respectively the densities 7·87 and 4·20, whence approximately Ta<sub>2</sub>O<sub>5</sub> = 53·4, and Nb<sub>2</sub>O<sub>5</sub> 31·4 per cent., giving for the oxygen-ratio of the acid and basic oxides,

$$\text{Ta} : \text{Nb} : \text{R} = 77 : 26 : 10,$$

and leading to a formula in which the molecular ratio of

$$\text{Nb}_2\text{O}_5 : \text{Ta}_2\text{O}_5 = 1 : 1.$$

In Dana's Mineralogy the ratios given are Nb<sub>2</sub>O<sub>5</sub> : Ta<sub>2</sub>O<sub>5</sub> = 2 : 1, 3 : 1, and 4 : 1. In accordance with the above analysis, the density of the mineral is greater than that of any of the specimens whose analyses are quoted by Dana.

*Orthite* occurs in the same locality in blade-like crystals several inches long, and with partly decomposed faces. Hardness, 5·5. Sp. gr. 3·323. Lustre pitchy. Colour greyish-black. Streak, greenish-grey. Fuses with much intumescence, and is gelatinised by hydrochloric acid at ordinary temperatures. Its analysis gave—

SiO <sub>2</sub> .....	32·35	FeO .....	10·48
Al <sub>2</sub> O <sub>3</sub> .....	16·42	MnO .....	1·12
Fe <sub>2</sub> O <sub>3</sub> .....	4·49	CaO .....	11·47
Ce <sub>2</sub> O <sub>3</sub> .....	11·14	K <sub>2</sub> O } .....	0·46
La <sub>2</sub> O <sub>3</sub> .....	3·47	Na <sub>2</sub> O } .....	
Di <sub>2</sub> O <sub>3</sub> .....	6·91	H <sub>2</sub> O .....	2·31
			100·62

*Monazite* from the same locality was found to contain thorium, a constituent not hitherto found in this mineral. Its analysis gave—

Ce <sub>2</sub> O <sub>3</sub> .	Di <sub>2</sub> O <sub>3</sub> .	La <sub>2</sub> O <sub>3</sub> .	Y <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .
16·30	24·4	10·3	1·1	0·9
Al <sub>2</sub> O <sub>3</sub> .	ThO <sub>2</sub> .	P <sub>2</sub> O <sub>5</sub> .	SiO <sub>2</sub> .	
0·04	18·6	24·04	2·7 = 98·38	

Excluding the thorium and silica, the remaining constituents give approximately the formula (R<sub>2</sub>)<sup>vi</sup>P<sub>2</sub>O<sub>8</sub>, the thorium being perhaps in the form of orangite.

H. W.

**Chemical Composition of the Minerals of the Cryolite Group.** By J. BRANDL (*Annalen*, **213**, 1—15).—This paper contains an account of the results obtained on analysing several of these minerals, which were obtained from Professor Groth, who had previously determined their crystalline form. The bases were determined in the solutions obtained by heating the finely powdered mineral with concentrated sulphuric acid, and for the determination of fluorine, Fresenius' modification (*Zeits. Anal. Chem.*, **5**, 190) of Wöhler's method was adopted with some slight alterations. The water in the majority of cases was determined directly by heating the mineral with lead oxide, and collecting the water in a calcium chloride tube.

*Cryolite.* A crystalline variety of this mineral was used; it belongs to the monosymmetric system, and has the same composition as the ordinary variety, viz.,  $\text{AlF}_3 \cdot 3\text{NaF}$ .

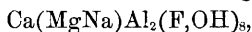
*Pachnolite* crystallises in thin monosymmetric needles, united in twin forms of an apparently rhombic habit; it occurs in cavities of thomsenolite; the analysis shows it to have the composition  $\text{AlF}_3 \cdot \text{CaF}_2 \cdot \text{NaF}$ .

*Thomsenolite* occurs in a variety of forms, and has frequently been confounded with pachnolite: the specimen analysed consisted of colourless, transparent, right-angled parallelepipeds. In composition it differs from pachnolite by containing 1 mol. of water.

*Ralstonite* is a rare mineral, discovered by Brush (*Sill. Amer. J.*, **1871**, **7**, 30), it crystallises in regular octohedrons, and occurs in spathic iron ore associated with thomsenolite. From the analysis, the formula  $4\text{AlF}_3 + 3\text{Na}(\text{Mg}, \text{Ca})\text{F} + 3\text{H}_2\text{O}$  may be deduced, in which it is supposed that a portion of the sodium is replaced by magnesium and calcium.

*Chiolite* is found in a massive form, associated with cryolite, at Mask, in the Ural Mountains. Analyses of this mineral have led to different formulæ being assigned to it by different observers. It has also been found in well-defined transparent crystals by Koksharov, and from the analyses of specimens of this variety, the formula  $3\text{AlF}_3 + 5\text{NaF}$  is assigned to it by the author.

*Prosopile* was discovered by Scheerer (*Pogg. Ann.*, **90**, 315, and **101**, 361), who thought that it contained silicon. The author has been unable to discover this element in it, and assigns to it the formula



in which the hydroxyl is supposed to replace fluorine, a supposition which is supported not only by the percentage of hydrogen and oxygen, but also by the fact that the mineral does not lose weight, even at  $260^\circ$ .

*Fluellite*, discovered by Levy, and shown by Wollaston to contain aluminium and fluorine: its formula is probably  $\text{AlF}_3 + \text{H}_2\text{O}$ .

P. P. B.

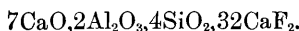
**Gunnisonite: a New Mineral from Colorado.** By F. W. CLARKE and N. W. PERRY (*Amer. Chem. J.*, **4**, 140—142).—This mineral, found in considerable quantity about twenty miles south of Gunnison in Colorado, is massive, easily scratched by the knife, and of deep purple colour both in mass and in powder. It is intimately



mixed with a semimassive calcite partly tinged with ferric oxide. Analysis of the mixture gave 31.96 F, 45.91 Ca, 6.02 SiO<sub>2</sub>, 5.21 Al<sub>2</sub>O<sub>3</sub> with trace of Fe<sub>2</sub>O<sub>3</sub>, 5.61 CO<sub>2</sub> and 0.74 Na<sub>2</sub>O = 93.45. The loss is oxygen, which must be reckoned as united with part of the calcium. Assuming that the fluorine and carbonic anhydride are wholly united with calcium, and recalculating the remainder of the calcium as oxide, the preceding results may be thus stated: 65.60 CaF<sub>2</sub>, 12.75 CaCO<sub>3</sub>, 10.02 CaO, 6.02 SiO<sub>2</sub>, 5.21 Al<sub>2</sub>O<sub>3</sub>, and 0.74 Na<sub>2</sub>O = 100.34, and lastly if the calcium carbonate be regarded as merely admixed calcite, the remaining numbers will give for pure gunnisonite—

CaF <sub>2</sub> .	CaO.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Na <sub>2</sub> O.
74.89	11.44	6.87	5.95	0.85 = 100

these numbers agreeing closely with the formula



The mineral is probably an alteration-product of fluor spar, although it may possibly be only a mixture of that species with a silicate.

H. W.

**Crystalline Rocks in the Neighbourhood of Messina.** By L. RICCIARDI (*Gazzetta*, 12, 203—206). This paper contains analyses of granite, gneiss, and mica-schist from the neighbourhood of Messina.

I, granite; II, gneiss; III, mica-schist. The powder of all of them when moistened was sensibly alkaline to litmus.

	I.	II.	III.
SiO <sub>2</sub> .....	74.09	70.57	57.67
Al <sub>2</sub> O <sub>3</sub> .....	15.13	17.96	17.92
FeO .....	2.33	1.25	9.10
CaO .....	2.92	5.17	3.19
MgO .....	0.97	1.51	3.29
Cl .....	trace	trace	trace
K <sub>2</sub> O .....	2.34	2.03	3.86
Na <sub>2</sub> O .....	0.85	0.77	1.09
P <sub>2</sub> O <sub>5</sub> .....	0.41	0.32	0.38
Loss on ignition ....	0.70	0.83	3.19
	99.74	100.41	99.69
Sp. gr. at 18° .....	2.63	2.66	2.88

C. E. G.

**Origin of Volcanic Ashes, and Chemical Composition of the Lavas and Ashes ejected in the latest Eruptions of Vesuvius (1868—1882).** By L. RICCIARDI (*Gazzetta*, 1882, 305—328).—This paper gives a summary of the views of various authors on the formation of volcanic ashes, and analyses of the lavas, sands and ashes ejected from Vesuvius in the interval 1868 to 1882. The following table shows the maximum and minimum values of the several constituents of these sands and lavas:—

Sands.			Lavas.	
SiO <sub>2</sub> .....	45·91	to 48·27	47·43	to 48·83
SO <sub>3</sub> .....	0·04	0·08	0·00	0·15
P <sub>2</sub> O <sub>5</sub> .....	1·65	2·65	1·83	2·12
Cl .....	0·02	0·06	traces	
Al <sub>2</sub> O <sub>3</sub> .....	15·11	18·65	15·58	to 19·58
Fe <sub>2</sub> O <sub>3</sub> .....	6·06	8·41	3·93	7·39
FeO .....	3·01	6·31	3·34	4·56
CaO .....	9·61	15·78	9·12	13·63
MgO .....	4·03	5·58	3·12	4·65
K <sub>2</sub> O .....	2·73	6·27	3·68	6·27
Na <sub>2</sub> O .....	1·02	1·77	1·41	2·47
Loss by ignition ..	1·30	3·67	0·12	1·41

The conclusions drawn from these analyses and from the study of the minerals of which the lava, sand, and ashes are composed, are as follows:—

1. The ashes are produced by disintegration of the lavas resulting from the action of aqueous vapour disengaged from the semifluid mass.

2. The lava consists of crystals formed in the interior of the mountain, and of an amorphous, often vitrified mass, either interposed between the several minerals, or including them within itself.

3. The salammoniac in volcanic products is formed partly by direct combination of nitrogen with hydrogen, partly by the combustion of organic substances overflowed by the lava.

4. The metallic sulphides in the ashes and lavas are formed by the action of hydrogen sulphide on metallic oxides.

5. The phosphoric acid in these volcanic products is in combination with lime. Only a small proportion of it is, however, in the form of apatite, the remainder of the calcium phosphate entering into the composition of the amorphous substances.

H. W.

**Waters of the Isthmus of Panama.** By AILLAUD (*Compt. rend.*, 95, 104—106).—This paper contains analyses of the water of two deep wells at Emperador, 50 kilometers from the northern extremity of the canal, and of the Rio Grande, which flows into the Pacific to the south of the town of Panama. The water of one of the wells is of good quality, the other is somewhat rich in organic matter. The river water furnishes a good potable water. It contains, however, 0·057 gram silica per litre, and also traces of ruthenium.

C. H. B.

**Analysis of the Oberbrunnen Springs at Salzbrunn in Silesia.** By R. FRESENIUS (*J. pr. Chem.* [2], 25, 310—320).—The waters of these springs have been analysed with great completeness of detail, at the request of the proprietor. Compared with an analysis made in 1866 by Dr. Valentiner the composition appears to be uniform. The water is in great demand for drinking at the wells and for export in bottles. The following is contained in 1000 grams of the water:—

	Valentiner, 1866.	Fresenius, 1881.
Sodium carbonate.....	1·5294	1·521213
Lithium carbonate .....	0·0075	0·008180
Sodium sulphate .....	0·4773	0·459389
Potassium sulphate .....	0·0268	0·052829
Sodium chloride .....	0·1719	0·176658
Calcium carbonate .....	0·2951	0·304345
Strontium carbonate .....	0·0033	0·003405
Magnesium carbonate .....	0·2902	0·311065
Ferric carbonate .....	0·00022	0·004137
Alumina and phosphoric acid..	0·0005	—
Silicic acid.....	0·0255	0·030750
	<hr/>	<hr/>
	2·82772	2·871971
Carbonic acid, semi-combined..	0·0220	0·935715
Carbonic acid, free .....	1·2430	1·876571

J. F.

## Organic Chemistry.

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**Some Reactions of Ethylene Bromide.** By F. BEILSTEIN and E. WIEGAND (*Ber.*, **15**, 1368—1370).—On heating ethylene bromide with silver oxide and water, aldehyde and a small quantity of silver acetate are produced, but if silver carbonate is substituted for the oxide, glycol is formed. When silver carbonate, ethylene bromide, and benzene are heated at 55°, a dark heavy oil is produced.

By the action of silver sulphate on ethylene bromide diluted with benzene, bromethyl sulphate is obtained as a heavy oil, which is decomposed by boiling with water, forming bromethylsulphuric acid. This acid afterwards splits up into sulphuric acid, hydrobromic acid and glycol. The crystalline barium salt is also very unstable. On warming a solution of the salt, barium sulphate is deposited, and glycol is formed. This salt does not appear to be identical with the barium salt of the acid, which Wroblewsky (*Zeitschr. f. Chem.*, 1868, 563) obtained by the action of fuming sulphuric acid on ethylene bromide.

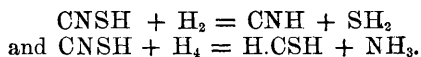
Silver sulphate does not act on ethylene chloride in presence of water at 100°. No reaction takes place between ethylene bromide and silver sulphite at 55° in the presence of water. W. C. W.

**Products of the Distillation of Colophony.** By A. RENARD (*Compt. rend.*, **95**, 141—142; see also Abstracts, 1881, 738, and this vol., 64, 737).—The fraction boiling between 106 and 156° is relatively very small. It contains a higher homologue of heptene, *octine*,  $C_8H_{14}$ , b. p. 129—132°; vapour-density 4.04; sp. gr. at 20° = 0.8158; soluble

in alcohol and ether. Octine absorbs oxygen somewhat rapidly, but has no action on ammoniacal solutions of cuprous chloride or silver nitrate. It reacts violently with bromine, giving off hydrobromic acid, but if the hydrocarbon is added drop by drop to bromine in excess, allowed to stand 24 hours, and the product is washed with soda and treated with ether, it yields crystals of a tribromo-derivative,  $C_8H_{11}Br_3$ , m. p.  $246^\circ$ , very slightly soluble in ether. The ethereal washings when evaporated leave a heavy orange-coloured oil, of the same composition as the crystals. If an ethereal solution of octine is added to an ethereal solution of bromine, a very unstable dibromide,  $C_8H_{14}Br_2$ , is formed. Nitric acid acts very violently on the hydrocarbon, with evolution of carbonic anhydride free from nitrous vapours, and formation of oxalic acid, succinic acid, and resinous products, which dissolve in the concentrated acid. By treatment with sulphuric acid, octine is polymerised with development of heat, but without evolution of sulphurous anhydride or formation of an appreciable quantity of sulphonic acid. When treated with hydrochloric acid gas, octine, alone or in ethereal solution, is altered and turns brown, but yields no definite hydrochloride. C. H. B.

**Action of Hydrogen on Thiocyanic Acid, and Decomposition of the Thiocyanates in the Residues from Gas Manufacture.**

By F. SESTINI and A. FUNARO (*Gazzetta*, **12**, 184—190).—Hofmann has examined the action of nascent hydrogen on thiocyanic acid, and found that it gave rise to the simultaneous formation of ammonia, thiomethaldehyde, methylamine, hydrocyanic acid and hydrogen sulphide; explaining the reaction by the following equations:—



The author finds that when potassium thiocyanate is treated with zinc and very dilute sulphuric acid in the cold, the odour of hydrocyanic acid and hydrogen sulphide soon becomes apparent, but even after the action has continued for two hours, there is no odour of the thioaldehyde, and the quantity of ammonia in the solution as sulphate is quite inappreciable; this would not be the case if the two reactions took place simultaneously as Hofmann supposed. On the contrary, when the action of the nascent hydrogen on the thiocyanic acid is continued for a long time and assisted by a gentle heat, thiomethaldehyde is produced, and the solution yields abundance of ammonia when boiled with potash after removal of the hydrocyanic acid and hydrogen sulphide.

It remained, therefore, to ascertain in what way the thiomethaldehyde is produced: two reactions are possible, methylamine formed by the action of nascent hydrogen on the hydrocyanic acid might react with hydrogen sulphide to give thiomethaldehyde and ammonia, or the thioaldehyde might be derived from carbon bisulphide by the action of nascent hydrogen. Experiment showed that the first hypothesis was inadmissible, as no trace of thioaldehyde was formed by allowing hydrogen sulphide and methylamine to remain in contact

under the most varied conditions. When thiocyanic acid is treated with an acid, it evolves hydrogen sulphide, and this, reacting with another portion of the thiocyanic acid, may give rise to carbon bisulphide and ammonia thus:  $\text{CNSH} + \text{H}_2\text{S} = \text{CS}_2 + \text{NH}_3$ , and it was found on digesting potassium thiocyanate with dilute sulphuric acid in a flask furnished with a reflux condenser, that carbon bisulphide is produced. The author infers, therefore, that the action of nascent hydrogen on thiocyanic acid takes place in one way only ( $\text{CNSH} + \text{H}_2 = \text{CNH} + \text{H}_2\text{S}$ ), and that the other products are the result of secondary reactions.

*Utilisation of Residues from Gas Manufacture.*—The lime which is used in the purification of gas contains ammoniacal salts which are valuable as fertilisers, but at the same time there are other substances present which are injurious, such as calcium sulphide and thiosulphate, bituminous matters, and especially ammonium thiocyanate. The author takes advantage of the readiness with which the last is decomposed by nascent hydrogen to remove it. The lime-waste is first spread out and exposed to the air for a time, by which the sulphides and thiosulphates are oxidised, and the bituminous matters become insoluble: the waste is then agitated for some time with twice its bulk of water, allowed to settle for five or six days, and the clear liquid decanted and treated with iron and sulphuric acid. In this way the thiocyanate is gradually decomposed, and after two or three days it is poured back on to the lime sludge, which precipitates the iron as oxide. When the iron is peroxidised, which soon takes place, it is ready for use. C. E. G.

**Action of Halogens on Sacchulmic Compounds.** By F. SESTINI (*Gazzetta*, 1882, 292—302).—I. When bromine-water holding in suspension sacchulmic acid or sacchulmin (Abstr., 1880, 538; this vol., 605), or the mixture of the two called sacchulmose, is agitated, an orange-yellow body is formed in a few hours if the original substance is freshly prepared and still moist, in two or three days if it has been dried. The product thus formed is an amorphous powder, insoluble in water, nearly insoluble in ether, somewhat more soluble, especially with the aid of heat, in absolute alcohol, to which it imparts a brownish-red colour. The increase in weight of the product is greater than that of the bromine absorbed, so that it is probable that the elements of water are likewise taken up in its formation. The alcoholic solution filtered at the boiling heat deposits a small quantity of yellow amorphous matter, and when evaporated to a tenth of its bulk, changes to a brown liquid which dries up to a black shining substance.

The product obtained as above has the same composition whether prepared from sacchulmic acid or from sacchulmin. Its analysis gave 38.0 to 38.14 per cent. carbon, and 2.86 to 3.04 hydrogen, agreeing nearly with the formula  $\text{C}_{22}\text{H}_{18}\text{Br}_3\text{O}_{11}$ , according to which its formation from sacchulmic acid,  $\text{C}_{11}\text{H}_{10}\text{O}_4$ , may be represented by the equation  $2\text{C}_{11}\text{H}_{10}\text{O}_4 + 9\text{Br} + 3\text{H}_2\text{O} = 6\text{HBr} + \text{C}_{22}\text{H}_{18}\text{Br}_3\text{O}_{11}$ \*; and as it

\* This equation is incorrect; the quantities of hydrogen on the two sides do not agree.—H. W.

contains three atoms of bromine united with two sacchulmic acid residues, the author designates it by the name sesquibromoxy-sacchulmide.

II. *Action of Chlorine on Sacchulmic Acid*.—When this acid, stove-dried, finely pulverised and suspended in water, is subjected to the action of a slow stream of chlorine, five or six hours daily for a week, its colour changes from black to reddish-brown and ultimately to yellow. The product thus formed is easily separated from the liquid by decantation, and after being washed and dried, first over sulphuric acid, then at 60–100°, may be purified, although with considerable loss, by solution in alcohol and precipitation with water. It is more soluble in alcohol of 85° than in absolute alcohol, and the alcoholic solution leaves on evaporation a reddish-yellow amorphous body, which gives by analysis 42.74 per cent. carbon, 3.18 hydrogen, 23.74 chlorine, and 30.34 oxygen, agreeing nearly with the formula  $C_{11}H_2Cl_2O_6$ , which requires 42.99 C., 261 H., 23.13 Cl, and 31.23 O. Its formation is represented by the equation  $C_{11}H_{10}O_4 + 4Cl_2 + 2H_2O = 6HCl + C_{11}H_2Cl_2O_6$ ; and as it contains 2 atoms Cl and 2 atoms O more than sacchulmic acid, the author names it dichloroxysacchulmide. This body is thrown down by water from its alcoholic solution in yellow flocks, which the microscope shows to be made up of light yellow more or less spherical globules from  $\frac{1}{500}$  to  $\frac{3}{500}$  mm. in diameter. It dissolves in acetic acid, and is deposited from the solution as a thin transparent yellowish film. After drying in a vacuum, it may be heated to 100° without alteration, but if heated in the moist state, it gives off acid vapours. It begins to turn brown at 175°, but does not melt even at 200°, at which temperature however, it decomposes with copious evolution of hydrochloric acid. It dissolves with deep brown colour in a cold solution of normal sodium carbonate, and decomposes hot solutions of carbonates, the liquid, which has a blackish tinge, giving a flocculent precipitate with hydrochloric acid. By the action of boiling water, dichloroxysacchulmide is resolved into hydrochloric acid and a brown product, which will be made the subject of future investigation.

III. *Oxysacchulmic Acid*,  $C_{11}H_8O_6$ , is obtained by boiling dichloroxy-sacchulmide with aqueous potash in a reflux apparatus for three hours, then leaving the liquid to cool, and gradually adding sulphuric acid till a slight acid reaction is perceptible, and the resulting precipitate after 20 hours' repose, is washed in a filter with cold water. So long as the wash-water contains a considerable quantity of sulphuric acid, it passes through nearly colourless, but when the washing is nearly complete, the oxysacchulmic acid dissolves in the water in considerable quantity, and the filtrate becomes deeply coloured. To recover the acid thus dissolved, the filtrate may be treated with cupric sulphate, which throws down a copious brown flocculent precipitate of cupric oxysacchulmate. This salt gives by analysis numbers agreeing nearly with the formula  $C_{44}H_{30}CuO_{24}$ , and showing that the acid has the composition  $C_{44}H_{32}O_{24}$ , or  $C_{11}H_8O_6$ .

IV. *Action of Chlorine on Sacchulmin*.—When this substance, which differs in composition from sacchulmic acid only by a small quantity of the elements of water, is treated with chlorine in the manner

already described with reference to the sacchulmic acid, it yields the same chlorinated product, viz., dichloroxysacchulmide.

V. *Action of Nascent Chlorine on Sacchulmose*.—When this substance, which is a mixture of sacchulmic acid and sacchulmin, is treated with a mixture of potassium chlorate and strong hydrochloric acid, chlorine is abundantly evolved; and if the mixture be gently heated, the sacchulmose becomes converted into a light yellow substance, which, after washing and drying, gives by analysis 32·27 per cent. chlorine, agreeing nearly with the formula of trichloroxysacchulmide,  $C_{11}H_8Cl_3O_6$ , which requires 32·07 per cent. Cl. This substance, like dichloroxysacchulmide, when subjected to the slow action of boiling water, gives up part of its chlorine; in contact with alkaline solutions, it emits an odour of chloroform and is converted into a product similar to, if not identical with, oxysacchulmic acid.

The results above detailed lead to the following conclusions:—

(1.) The halogens afford the means of uniting an additional quantity of oxygen to the elements of a molecule of an ulmic product, and thus obtaining substances which may be regarded as products of oxidation obtained through the medium of compounds containing chlorine and bromine, the study of which substances may lead to important extensions of our knowledge of the chemical nature of ulmic compounds.

(2.) By the action of the halogens, it may be possible to arrive at the quantitative estimation of ulmin, a substance which has hitherto resisted the action of all solvents, and consequently has never yet been separated from the other bodies with which it is mixed in peat, soil, &c.

H. W.

**Elementary Composition of Starch.** By F. SALOMON (*J. pr. Chem.* [2], 25, 348—362).—The experimental results on this subject being of a contradictory nature, and the important question as to the composition of starch not being as yet satisfactorily answered, the author has made it the subject of a very extensive series of experiments. Before starting the ultimate experiments, he made a careful analysis of the starch used, by the method described in the *Repert. f. Anal. Chemie*, 1, 274, and made a series of preliminary experiments to study the properties of the starch-sugar, already published (*ibid.*, 309). In one experiment he found that the sugar itself underwent a change by boiling with sulphuric acid, which, however, did not alter the polarisation, but made a difference in the reducing power as regards Fehling's solution (after four hours' boiling with dilute acid [1:19] the loss = 4·95 per cent.); he thinks this the cause of Allihn's small yields of sugar. The potato-starch employed in these experiments contained 76·50 per cent. pure starch, 0·247 residue insoluble in dilute acid, 0·273 ash, 22·980 water. The following method of conversion is employed: 3 grams of air-dried starch are mixed in a flask with 200 c.c. water and 20 c.c. hydrochloric acid (sp. gr. 1·125). The flask (fitted with a reflux condenser for the polarisation experiments) is heated in a water-bath for three hours. Sufficient potash is then added to nearly neutralise the acid, the solution made up to a definite volume, and the sugar determined by Allihn's method; the results ob-



tained agree with those of Allihn, the mean of six experiments (three of the author's and three of Allihn's) showing that sugar formed = 111.16 per cent. of the starch employed. In addition, he has made several determinations of the sugar by taking the sp. gr., and the rotatory power, and with similar results. In the polarisation experiments, he arranges that the sugar solutions should always be of about the same degree of concentration. The results tend to show that  $C_6H_{10}O_5$  really represents the composition of potato-starch: for the equation  $C_6H_{10}O_5 + H_2O = C_6H_{12}O_6$ , requires that 100 parts of pure dry starch should yield 111.11 parts of sugar. The author thinks it probable that all starches are not alike, differing as they do in their physical and chemical properties; for instance, wheat-starch behaves differently from potato-starch with iodine solution, and according to Sachsse gives higher results on conversion into sugar.

The method of conversion described above is advantageous on account of the moderate temperature, quickening the conversion by the use of stronger acid, and the avoidance of high pressure.

D. A. L.

**Nitration of Cellulose.** By VIEILLE (*Compt. rend.*, **95**, 132—135).—The cellulose used was in the form of cotton-wool. The lowest nitration product, mononitro-cellulose, is obtained by the action of nitric acid of sp. gr. 1.450. It is insoluble in ethyl acetate and in a mixture of alcohol and ether: analysed by Schloesing's method, 1 gram yields 108.9 c.c. of nitric oxide. A nitration product, soluble in a mixture of alcohol and ether, and therefore suitable for making collodion, is given only by acid of sp. gr. between 1.490 and 1.496. It retains the structure of the original cotton, and is entirely soluble in ethyl acetate; 1 gram yields 183—194.4 c.c. of nitric oxide. The time required to produce the maximum nitration with acid of a particular strength is longer the weaker the acid, 2 to 3 hours sufficing with acid of sp. gr. 1.50, whilst acid of 1.483 requires 120 hours. With acid of sp. gr. 1.470, however, the cotton swells up and dissolves immediately, and under these conditions nitration is rapid: when the syrupy solution is poured into water, a white precipitate, which has none of the structure of the original cotton, is thrown down. Acid of sp. gr. 1.460 acts only slowly on cotton, but the fibres become very brittle, and the product is collected in the form of a pulp. Weaker acid has little or no action on cotton. The maximum nitration is obtained with a mixture of nitric and sulphuric acids. The result is not sensibly affected by the relative proportions of the two acids, even if Nordhausen sulphuric acid is used, but a large excess of sulphuric acid considerably diminishes the rapidity of the reaction. The product has the composition  $C_{24}H_{29}(NO_2)_{11}O_{20}$ , retains the appearance of the original cotton, is completely soluble in ethyl acetate, but only very slightly soluble in a mixture of alcohol and ether. 1 gram yields 214 c.c. of nitric oxide.

C. H. B.

**Nitrogenous Acetone Derivatives.** By V. MEYER and A. JANNY (*Ber.*, **15**, 1164—1167).—By heating unsymmetrical dichloroacetone with hydroxylamine hydrochloride (6 mol.) in aqueous solution, and an

equivalent amount of soda, *acetoximic acid*,  $C_3H_5N_2O_4$ , is obtained. It crystallises from alcohol in small transparent prisms melting at  $153^\circ$ , and from water in small cauliflower-like masses; it exhibits acid properties, and dissolves in alkalis to a colourless liquid. The silver salt,  $C_3H_5AgN_2O_4$ , is obtained as a white precipitate. When boiled with strong hydrochloric acid, hydroxylamine hydrochloride is formed in considerable quantity. Acetoximic acid can also be obtained by the action of nitrosoacetone on hydroxylamine. The authors consider the probable constitution of acetoximic acid as  $NO.CH_2.CMe:N.OH$ , and that the nitrogen in nitrosoacetone may also be present as an oximide-group ( $=N-OH$ ).

A. J. G.

**Action of Electrolytic Hydrogen on Bibasic Acids of the Paraffin Series.** By L. BALBIANO and A. ALESSI (*Gazzetta*, **12**, 190—195).—In these experiments the authors employed Naudin's copper-zinc couple (*Bull. Soc. Chim.*, **36**, 273), and Gladstone and Tribe's couple, the zinc and copper being in the proportions 3:1, but the zinc foil was about three times the thickness employed by them.

Oxalic acid in 5 per cent. aqueous solution, submitted to the action of Naudin's couple at  $100^\circ$  for 12 hours, gave glycollic acid amounting to about 7 per cent. of the theoretical quantity. Neutral sodium oxalate, in 2 per cent. aqueous solution with Gladstone and Tribe's couple at  $100^\circ$  for 20 to 30 hours, also gave glycollic acid, but only about 1.5 per cent. of the amount indicated by theory. The calcium glycolate obtained from oxalic acid crystallised with 5 mols.  $H_2O$ , whilst that from sodium oxalate crystallised with 4 mols.  $H_2O$ . Claus (*Bull. Soc. Chim.*, 1867, p. 358) disputes Church's statement that the action of nascent hydrogen on succinic acid gives rise to an alcoholic acid: it seemed to be a matter of interest therefore to ascertain the action of the zinc couple on neutral sodium succinate. The results were negative; no other acid except succinic could be detected in the solution.

C. E. G.

**Formation of Acid Chlorides by aid of Sulphuric Hydroxy-chloride.** By K. HEUMANN and P. KOCHLIN (*Ber.*, **15**, 1114—1119).—By the action of sulphuric hydroxychloride,  $SO_2(OH)Cl$ , on potassium chromate, chromyl chloride was obtained, but a considerable quantity of the chromium remained in the retort as an insoluble green mass. This insoluble substance owes its formation to a reaction between chromyl chloride and sulphuric hydroxychloride.

Hydrochloric acid gas reacts on dry chromic anhydride, converting it into chromyl chloride, much heat being evolved.

Acid chlorides are not formed by the action of sulphuric hydroxychloride on organic acids, or are formed in small quantity only, the main reaction being the formation of sulphochlorides. In the action of sulphuric hydroxychloride on aromatic hydrocarbons, sulphonic acids and sulphochlorides are obtained; the authors regard the formation of the first as the normal reaction, and consider the formation of the sulphochloride to be due to the action of the sulphuric hydroxychloride on the sulphonic acid first formed.

A. J. G.

**Occurrence of a New Fat Acid in the Nut of the California Bay Tree.** By J. M. STILLMAN and E. C. O'NEILL (*Amer. Chem. J.*, **4**, 206—211).—This tree, *Umbellularia californica* (otherwise known as *Oreodaphne*, *Tetranthera*, or *Laurus californica*) is one of the most widely distributed, as well as one of the largest and handsomest of the valley trees of California. It is evergreen; its wood is much used as an ornamental wood in cabinet-work. The leaves when crushed have a strong and pungent odour, very pleasant however, when not too strong. The same odour, but fainter, is present in the wood when freshly cut. The fruit, which is abundant, consists of a berry somewhat larger than the olive, and of about the same shape, enclosing a smooth seed something smaller than an olive. The seed or nut has a thin hard shell and a large dry kernel.

The nuts divested of their fleshy husks and shells were well ground in a mortar, and digested with ether, in a percolating apparatus, and the ether was then distilled off, leaving the pure fat, which solidified on cooling to a hard tallowy mass melting at  $31^{\circ}$  to  $32^{\circ}$ , and having in the melted state a sp. gr. of 0.925 at  $31^{\circ}$ . Its taste is disagreeable, producing irritation in the throat, due perhaps to the presence of a certain quantity of free acid. The fat dissolves readily in ether and in benzene, but only sparingly in alcohol.

By saponifying this fat with caustic potash and decomposing the resulting soap-solution with hydrochloric acid, washing the clear oily layer which separates on the surface with hot water, then separating and drying it, a white tallowy mass is obtained, smelling faintly when cold, but emitting a peculiar, disagreeable, irritating odour when heated. Its melting point varied in different preparations from  $31^{\circ}$  to  $34^{\circ}$ , and its analysis gave 71.24 per cent. carbon and 11.91 hydrogen. Further, by fractionally precipitating an alcoholic solution of this acid with alcoholic magnesium acetate, then saturating the mixture with ammonia, leaving it at rest, decomposing the resulting magnesium salts with hydrochloric acid, and analysing the fractions of acid thus obtained, it was found that the fatty acid of the nut consists mainly of a member of the acetic series having the composition  $C_{11}H_{22}O_2$ . This acid, the authors designate as *umbellulic acid*. When purified as completely as possible, it is a white crystalline solid of peculiar taste, which irritates the mucous membranes of the throat. It distils at ordinary pressures without decomposition, giving a limpid distillate which solidifies to a crystalline mass on cooling. It boils at  $270$ — $275^{\circ}$  (uncorrected) under ordinary pressure, and at  $208$ — $211^{\circ}$  under a pressure of 100 mm. [Krafft's undecylic or undecic acid, having the same composition, boils at  $212$ — $6^{\circ}$  under 100 mm. pressure (*Ber.*, **11**, 2219; **12**, 1667)].

The methyl-, ethyl-, and amyl-ethers of umbellulic acid, prepared in the usual way by passing dry hydrogen chloride into solutions of the acid in the corresponding alcohols, are mobile fragrant liquids, the first boiling (after purification by fractional distillation) at  $244^{\circ}$  to  $246^{\circ}$ , the second at  $253$ — $255^{\circ}$ , and the third at about  $295^{\circ}$ .

H. W.

**Dibromacrylic and Tribromopropionic Acids.** By H. B. HILL and C. W. ANDREWS (*Amer. Chem. J.*, **4**, 177—183).—An abstract

of the first part of this paper, describing the dibromacrylic acid obtained by decomposing barium tribromopropionate with hydrochloric acid, has already been given in this Journal (Abstr., 1881, p. 1030).

*Tribromopropionic acid*,  $C_3H_3Br_3O_2$ .—When dibromacrylic acid prepared by the action of barium hydroxide on mucobromic acid is heated for eight or ten hours at  $100^\circ$  in sealed tubes with three or four times its weight of hydrobromic acid, the needle-like crystals disappear and are replaced by rectangular plates of tribromopropionic acid, easily purified by successive recrystallisation from light petroleum and carbon bisulphide. The acid thus prepared is very soluble in alcohol and ether, somewhat less soluble in chloroform, carbon bisulphide, benzene, and light petroleum. It dissolves freely in hot water, but on boiling the solution it is rapidly decomposed, with formation of hydrobromic acid. After repeated crystallisation from carbon bisulphide, the acid melts at  $118^\circ$ . The *silver salt*,  $C_3H_2AgBr_3O_2$ , is obtained by precipitation from a cold aqueous solution of the acid, in small clustered rhombic plates. It is rapidly decomposed by warming with water, with formation of silver bromide, but may be dried over sulphuric acid, without essential decomposition. The barium and calcium salts dissolve readily in cold water, but the solutions are instantly decomposed on warming, with formation of bromide. The barium salt is likewise almost wholly decomposed when its solution is evaporated over sulphuric acid in a vacuum at ordinary temperatures; the calcium salt appears to be somewhat more stable, as it was obtained by similar treatment in dendritic groups of needles; the mother-liquor however contained calcium bromide.

The dibromacrylic acid,  $C_3H_2Br_2O_2$ , obtained by treating this tribromopropionic acid with barium hydroxide, agrees in melting point ( $85$ – $86^\circ$ ) and all its other properties with that which is prepared from mucobromic acid.

H. W.

**Crystalline Forms of Manganese Tartronate and of Tartronic Acid as given by D. Pantanelli.** By R. PANEBIANCO (*Gazzetta*, 12, 183).—This is a note by Panebianco on Pantanelli's measurements of the crystals of these compounds, in which he points out various errors and inconsistencies.

C. E. G.

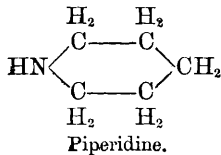
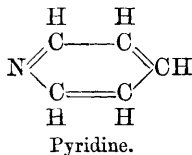
**Synopsis of the Polybasic Fatty Acids obtained from Malonic Acid by Conrad's Method.** By C. A. BISCHOFF (*Ber.*, 15, 1109–1111).

Name and formula of acid.	M. p. of acid.	Normal ethyl salt, b. p.	Decomposes into 1 mol. CO <sub>2</sub> .	Described in Abstract.
Malonic acid..... Methenyltricarboxylic acid (formyltricarboxylic acid).	132° —	196° 257° (144° at 90 mm.).	Acetic acid. Malonic acid, m. p. 132°.	— 1879. 707, 918.
Ethenyltricarboxylic acid.....	159°	278° (172° at 90 mm.).	Succinic acid, m. p. 180°.	1881. 156.
$\beta$ -Methylethenyltricarboxylic acid (propenyltricarboxylic acid).	146°	270° (178° at 90 mm.).	Pyrotartaric acid, m. p. 112°.	1881. 156, 579.
$\alpha$ -Propylethenyltricarboxylic acid.	148°	280°	Propylsuccinic acid, m. p. 91°.	1882. 948.
$\alpha$ -Isopropylethenyltricarbo- xylic acid.	—	—	Isopropylsuccinic acid, m. p. 114°.	1882. 948.
Acetylenetetetracarboxylic acid.	—	305° m. p. 75°	Ethenyltricarboxylic acid, m. p. 159°.	1880. 629.
Dicarbotetracarboxylic acid..	Syrup decomposing at 60°.	328° (210° at 90 mm.), m. p. 57°.	—	1881. 169.
Isallylenetetetracarboxylic acid.	151°	295° (200° at 90 mm.).	Tricarballic acid, m. p. 158°.	1881. 156.
Propargylpentacarboxylic acid.	—	323° (275—280° at 90 mm.)	—	1882.

**Ethyl Cyanomalonate.** By A. HALLER (*Compt. rend.*, **95**, 142—145).—Ethyl malonate was prepared by Conrad's method (*Annalen*, **204**, 126). 32 grams of the ether were mixed with a solution of 4.6 grams sodium in 50 grams absolute alcohol, and a current of dry cyanogen chloride passed into the homogeneous mixture until it was no longer absorbed. There is considerable development of heat, and the reaction should be moderated by placing the vessel in cold water. After saturation with cyanogen chloride, the thick yellow liquid is diluted with water and agitated with ether, to remove alcohol and unaltered ethyl malonate. The aqueous solution is acidified and again agitated with ether. On evaporation of the ethereal solution, *ethyl cyanomalonate* is obtained as a reddish liquid with a distinctly acid reaction. It is dissolved in sodium carbonate, filtered, reprecipitated by addition of acid, washed with water, dried over calcium chloride, and distilled in a vacuum. Thus purified, ethyl cyanomalonate,  $\text{CN}.\text{CH}(\text{COOEt})_2$ , is a colourless oily liquid with a pungent smell and acid reaction, b. p.  $120\text{--}130^\circ$  at 25 mm., slightly soluble in water, to which it imparts an acid reaction, soluble in alcohol, ether, and alkaline solutions. It decomposes carbonates with evolution of carbonic anhydride, and when exposed to the air is coloured slightly red. Its formation may be expressed thus:  $\text{CHNa}(\text{COOEt})_2 + \text{CNCl} = \text{NaCl} + \text{CN}.\text{CH}(\text{COOEt})_2$ . The sodium, calcium, and lead salts of the general formula  $\text{CN}.\text{CM}(\text{COOEt})_2$  are obtained by the action of the ether on the corresponding carbonates. They are crystalline compounds soluble in water and alcohol, and resemble the metallic compounds obtained by the author and Held from ethylic acetoacetylacetate, and to be described in a subsequent paper. These salts also resemble the metallic derivatives obtained by different chemists from ethylic acetoacetate and chloracetoacetate. The derivatives of these ethers are, however, obtained by the direct action of the metals on the ethers, or by treating the latter with solutions of the metallic oxides in ammonia or potash, whilst the derivatives of ethyl cyanomalonate and acetoacetylacetate are obtained by their action on metallic carbonates. It would appear therefore that the introduction of the cyanogen group into the molecule of ethyl malonate and acetoacetylacetate, increases the readiness with which they exchange hydrogen for metals.

C. H. B.

**Transformation-products of Glutaric or Normal Pyrotartaric Acid.** By O. BERNHEIMER (*Gazzetta*, 1882, 281—285).—The object of the experiments described in this paper was to examine the derivatives of glutaric acid intermediate in composition between that acid and piperidine. Granting that piperidine is related to pyridine in the manner pointed out by Kœnigs (*Ber.*, **12**, 2341; **14**, 1856; this *Journal*, 1879, *Abstr.*, 403), and represented by the following formulæ:—



and that the imide of glutaric acid is a pyridine derivative having its nitrogen-atom and its five carbon-atoms linked together in a closed chain in the same manner as the piperidine, it follows that the replacement of the two oxygen-atoms in this imide by four atoms of hydrogen must lead directly to the formation of piperidine.

Glutaric acid, prepared by saponification of trimethylene cyanide, was converted into ammonium salt, and this salt, perfectly dried and finely pulverised, was heated in a retort placed in an oil-bath. It began to boil at  $150^{\circ}$ , and at  $175$ – $180^{\circ}$  gave off ammonia and water, and was converted into glutarimide,  $C_5H_7NO_2$ , which collected as a crystalline mass, partly in the neck of the retort, partly at the bottom. This product dissolves in boiling alcohol, and separates on cooling in very thin shining scales, which may be obtained perfectly colourless by recrystallisation from boiling alcohol, with addition of a small quantity of bone-black.

Glutarimide thus obtained melts at  $151$ – $152^{\circ}$ , and sublimes without alteration at a slightly higher temperature. It dissolves in water and in boiling benzene, but is nearly insoluble in ether. Like succinimide, it forms a silver-compound, which is obtained as a crystalline powder by boiling the alcoholic solution of the imide with ammoniacal silver nitrate and evaporating over sulphuric acid. This silver-compound, like that of succinimide, when heated in a sealed tube with methyl iodide, does not yield a methylated imide, but is reconverted into glutarimide. Glutarimide heated with zinc-dust gives off a large quantity of ammonia, and yields a hydrocarbon, together with a base which appears to be intermediate in composition between pyridine and piperidine.

Glutarimide is attacked by phosphorus pentachloride, slowly at ordinary temperatures, more quickly at  $50$ – $60^{\circ}$ , hydrochloric acid being abundantly evolved, and the mass being converted into a dark-coloured liquid, which, when shaken with light petroleum, separates into two layers, the lower containing unaltered glutarimide, while the upper, when evaporated over a water-bath, leaves a residue which becomes crystalline after all the phosphorus oxychloride has separated. On distilling this residue with steam, there passes over a very white crystalline body, which, when purified by crystallisation from dilute alcohol, has the composition  $C_5H_6Cl_3N$ , and appears to be con-

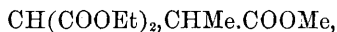
stituted according to the formula 
$$N \begin{array}{c} \text{CCl}_2 \quad \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CH}_2 \quad \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CCl} \quad \text{CH}_2 \end{array}$$
 inasmuch as when

heated at  $150^{\circ}$  in sealed tubes with hydriodic acid and amorphous phosphorus, it yields a product having nearly the composition of monochloropiperidine.

H. W.

**Occurrence of  $\alpha$ -Hydroxyglutaric Acid in Molasses.** By E. O. v. LIPPMANN (*Ber.*, **15**, 1156–1158).—The author has succeeded in isolating  $\alpha$ -hydroxyglutaric acid from the calcium sucrate obtained on the large scale in preparing sugar from molasses. The acid was identified by its melting point, by its analysis together with that of its zinc salt, and finally by conversion into glutaric acid. A. J. G.

**Tri- and Penta-basic Acids of the Paraffin Series.** By C. A. BISCHOFF and A. EMMERT (*Ber.*, **15**, 1107—1107), (cf. *Abstr.*, 1881, 156 and 579).—By the action of methyl  $\beta$ -chloropropionate on ethyl sodium malonate, *methylic diethylic propenyltricarboxylate*,



is obtained, b. p.  $268^\circ$ , sp. gr. 1.079 at  $17^\circ$ ; it resembles the triethyl salt, and on saponification with potash yields propenyltricarboxylic acid.

By the action of bromine on propenyltricarboxylic acid there has been obtained, in addition to the acids previously described, a *dibromopyrotartaric acid* (m. p.  $127\text{--}128^\circ$ ) differing from those already known; it dissolves in water, gives a white precipitate with lead acetate, and loses all its bromine when treated with silver nitrate and nitric acid.

By treating ethyl monochlorethenylcarboxylate with a 20 per cent. alcoholic solution of potash, salts of *ethoxyethenyltricarboxylic acid*,  $\text{OEt.C}(\text{COOH})_2\text{CH}_2\text{COOH}$ , are obtained.

*Ethylic propargylpentacarboxylate*,



is readily obtained by the action in the cold of 2—3 grams sodium, 50 grams absolute alcohol, and 27 grams ethyl chlorethenyltricarboxylate. It boils between  $275\text{--}280^\circ$  under 188 mm. pressure.

A. J. G.

**Solubility of the Different Modifications of Tartaric Acid in Water.** By E. LEIDIE (*Compt. rend.*, **95**, 87—90).—The curves of solubility of dextro- and lævo-tartaric acids are identical, and are represented by the same two parabolic equations of the second degree. The curve changes at  $40^\circ$ , and between  $40^\circ$  and  $100^\circ$  the increase of solubility with the temperature is less than between  $0^\circ$  and  $40^\circ$ . The identity of the two curves explains the impossibility of decomposing racemic acid by fractional crystallisation. The solubility of racemic acid is also represented by two parabolic equations of the second degree. The curve changes at  $35^\circ$ , but, unlike tartaric acid, the solubility increases more rapidly between this temperature and the boiling point of the solution ( $111^\circ$ ), than between  $0^\circ$  and  $35^\circ$ . The change of the curve between  $40^\circ$  and  $45^\circ$  in the case of the tartaric acids, and between  $30^\circ$  and  $35^\circ$  in the case of racemic acid, indicates that at these temperatures the three acids begin to be converted one into the other under the influence of heat and water. The following table gives the amount of the three acids dissolved by 100 parts of water at the particular temperatures:—



Tempera- ture.	Dextro- and lævo- tartaric acids.	Anhydrous racemic acid.	Hydrated racemic acid.
0°	115.04	8.16	9.23
5	120.00	10.05	11.37
10	125.72	12.32	14.00
15	132.20	14.97	17.07
20	139.44	18.00	20.60
25	147.44	21.41	24.61
30	156.20	25.20	29.10
35	165.72	29.37	34.09
40	176.00	37.00	43.32
45	185.06	43.31	51.16
50	195.00	50.00	59.54
55	205.83	57.07	68.54
60	217.55	64.52	78.33
65	230.16	72.35	88.73
70	243.66	80.56	99.88
75	258.05	89.15	111.81
80	273.33	98.12	124.56
85	289.50	107.47	138.19
90	306.56	117.20	152.74
95	324.51	127.31	168.30
100	343.35	137.80	184.91

C. H. B.

**Ethyl Acetoacetate.** By C. DUISBERG (*Ber.*, 15, 1378—1388).—Five atoms of hydrogen in ethyl acetoacetate can be successively replaced by bromine. The author denies the existence of ethyl acetoacetate dibromide,  $C_6H_{10}Br_2O_3$ , described by E. Lippmann (*Wien. Akad. Ber.*, 1868, 58 [ii], 310), also of ethyl dibromacetoacetate dibromide described by C. Conrad (*Ann.*, 186, 232).

*Monobromethyl acetoacetate*,  $C_6H_9BrO_3$ , is a dark brown liquid (sp. gr. 1.511 at 22°), freely soluble in alcohol and ether. It yields a cherry-red coloration with ferric chloride and a green crystalline precipitate with neutral copper acetate. *Copper ethyl monobromacetoacetate*,  $Cu(C_6H_8BrO_3)_2$ , is soluble in alcohol, ether, and carbon bisulphide. When heated, it is decomposed into copper bromide, alcohol, and probably monobromacetone.

*Dibromethyl acetoacetate* is a dark-coloured oil (sp. gr. 1.884 at 25°). With baryta-water the aqueous solution gives first a claret coloration, and afterwards a white precipitate. It resembles the monobromo-derivative in its behaviour with copper acetate.

*Tribromethyl acetoacetate*,  $C_6H_7Br_3O_3$ , has the sp. gr. 2.144 at 22°. It is decomposed by heat.

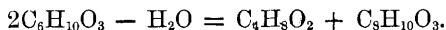
*Tetrabromethyl acetoacetate* is a red liquid, sp. gr. 2.401 at 17°. The pentabromo-compound is a brown liquid.

On the addition of alcoholic ammonia to monobromethyl acetoacetate, *ethyl hydroxytetrolate* is deposited in glistening needles (m. p. 127°) of a pale yellow colour. The crystals dissolve in ether and in hot alcohol, forming fluorescent solutions. With ferric chloride, the alcoholic solution gives a red coloration. A better yield of ethyl hydroxytetrolate is obtained by the action of sodium on a solution of mono-

bromethyl acetoacetate in anhydrous ether. The ethereal salt is saponified by treatment with dilute soda at the ordinary temperature. *Hydroxytetrollic acid*,  $C_4H_4O_3$ , crystallises in white needles soluble in alcohol and ether. The aqueous solution gives a blue coloration with ferric chloride. It is possible that these bodies are respectively identical with the "ethyl succinosuccinate" and "quinhydrone-dicarboxylic acid" described by F. Heermann (*Ann.*, **211**, 309).

*Paramidoethyl acetoacetate*, formed by the action of aqueous or alcoholic ammonia on ethyl acetoacetate, crystallises in monoclinic plates, soluble in alcohol and ether. This substance melts at  $20^\circ$ , and boils at  $213^\circ$ . Its sp. gr. at  $30^\circ$  is 1.014. By the action of an excess of hydrochloric acid, or sodium hydroxide, or by the action of water at  $150^\circ$ , it is split up into acetone, alcohol, ammonia, and carbonic anhydride. This compound is therefore identical with that described by Precht (*Ber.*, **11**, 1193), and is isomeric with the substance which Geuther obtained from ethylic ethylacetoacetate (*Jena Zeitschr.*, 1865, 404).

When ethyl acetoacetate is saturated with dry hydrochloric acid, and left at rest for some days, it decomposes into ethyl acetate and ethyl carbacetoacetate:



*Ethyl carbacetoacetate* is a thick liquid; sp. gr. 1.136 at  $27^\circ$ , b. p.  $290-295^\circ$ . The alcoholic solution of this ethereal salt does not yield any coloration with ferric chloride. W. C. W.

**Action of Fuming Nitric Acid on Ethyl Acetoacetate and Chloracetoacetate.** By M. PRÖPPER (*Ber.*, **15**, 1154).—A preliminary notice that the author has obtained ethyl nitrosoacetate and ethyl chloronitrosoacetate by these reactions. A. J. G.

**Alkines.** By A. LADENBURG (*Ber.*, **15**, 1143—1149).—*Benzoylpiperethylalkine* is obtained as hydrochloride by the action of benzoic chloride on piperethylalkine as a snow-white crystalline mass; on treatment with hydriodic acid or potassium iodide, it yields the hydriodide  $C_{14}H_{19}NO_2 \cdot HI$ , crystallising in brilliant plates. The platinochloride forms silky interlaced needles, the picrate can be crystallised from hot water.

*Phenylglycolylpiperpropylalkine* is prepared by repeated evaporation of an aqueous solution of piperpropylalkine mandelate with a little hydrochloric acid; the aurochloride,  $C_{16}H_{23}NO_3 \cdot AuCl_4H$ , is precipitated as an oil solidifying after some weeks to a compact crystalline mass.

*Acetyl piperpropylalkine* is obtained by the action of acetic chloride on piperpropylalkine; the aurochloride,  $C_8H_{16}NO\overline{Ac} \cdot AuCl_4H$ , is a crystalline precipitate.

*Cinnamyltriethylalkine* (*Ber.*, **14**, 1879) is obtained as chloride by the action of dilute hydrochloric acid on triethylalkine cinnamate. The aurochloride,  $C_{15}H_{21}NO_2 \cdot AuCl_4H$ , forms an oily mass soon becoming crystalline.

*Benzoylconylethylalkine* is prepared by the action of benzoic chloride on conylethylalkine as a white crystalline mass; with hydriodic acid, it gives a white curdy precipitate,  $C_{17}H_{26}NO_2 \cdot HI$ , which can be crystallised in white nacreous plates. A picrate and platinochloride are also obtainable.

Diethylpropylalkine unites with methyl iodide with explosive violence, yielding a solid substance nearly insoluble in water; after conversion into the chloride it gives a crystalline platinochloride,  $(C_{17}H_{17}NOMeCl)_2$ ,  $PtCl_4$ , and also a crystalline aurochloride.

*Piperpropylalkine iodide* is obtained by heating piperpropylalkine with hydriodic acid and amorphous phosphorus for some hours at  $140-150^\circ$ . It crystallises in long colourless prisms, sparingly soluble in cold, readily in hot water. Its composition is either  $C_8H_{19}NI_2$  or  $C_8H_{17}NI_2$ , the latter perhaps being the more probable; and corresponding to the constitution  $NHI(C_5H_{10})(C_3H_6I)$ . On treatment with silver chloride, all the iodine is replaced, and a readily soluble chloride obtained; this unites with auric chloride, yielding an oil which after a time solidifies to long plates of the composition  $C_8H_{19}NCl_2$ ,  $AuCl_3$  or  $C_8H_{17}NCl_2$ ,  $AuCl_3$ .

*Piperethylalkine iodide*,  $C_7H_{17}NI_2$  or  $C_7H_{15}NI_2$ , forms brilliant snow-white plates, readily soluble in hot water. Treated with silver chloride, it exchanges only one atom of iodine for chlorine, the resulting iodochloride yielding an aurochloride, crystallising in needles, and a platinochloride,  $(C_7H_{17}NiCl)_2PtCl_4$  or  $(C_7H_{15}NiCl)_2PtCl_4$ , crystallising in yellowish-red interlaced needles.

*Triethylalkine iodide*,  $C_6H_{17}NI_2$  or  $C_6H_{15}NI_2$ , crystallises in well-formed needles.

The great ease with which tropine is converted into tropidine suggested that similar substances to the latter alkidines would be obtained from the alkinines by the action of dehydrating agents, but no general method of preparing such bodies could be discovered. Piperpropylalkine is not affected by concentrated sulphuric acid; by heating with concentrated hydrochloric acid at  $170-180^\circ$  and saponifying with potash, a very small quantity of base (b. p.  $115-158^\circ$ ) was obtained, in which probably traces of alkidine were contained. By the action of hydriodic acid and amorphous phosphorus on piperpropylalkine, *propylpiperidine* (Abstr., 1881, 535) was obtained.

When triethylalkine is heated with amorphous phosphorus and hydriodic acid, it behaves quite differently; the product of the reaction after distillation with potash and neutralisation with hydrochloric acid gives with auric chloride a salt,  $C_6H_{13}N, AuCl_4H$ , crystallising in golden-yellow prisms (m. p.  $138-140^\circ$ ), and from this would appear to be an alkidine—*vinylldiethylamine*,  $N(C_2H_3)Et_2$ .

Piperpropylalkine iodide when distilled with potash, yields as the main product, *propylenedipiperidine*,  $C_{13}H_{26}N_2$ , a yellow oil distilling between  $300^\circ$  and  $315^\circ$ , insoluble in water, soluble in dilute hydrochloric acid, and yielding an aurochloride,  $C_{13}H_{26}N_2, 2AuCl_4H$ , and a platinochloride,  $C_{13}H_{26}N_2, PtCl_6H_2$ .

Triethylalkine iodide digested with moist silver oxide and distilled gives a strongly alkaline liquid, probably *ethylenetetrethylidiamine*,  $N_2Et_4(C_2H_4)$ , the aurochloride having the formula  $C_{10}H_{24}N_2, 2AuCl_4H$ .

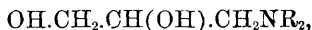
A. J. G.

**Glycolines and Glycoleines.** By C. F. ROTH (*Ber.*, 15, 1149—1154).—*Piperpropylglycoline*,  $C_8H_{17}NO_2$ , is prepared by heating chlorhydrin and piperidine in molecular proportion for 6—8 hours at  $100^\circ$ , and subsequently treating the product with potash. It forms colourless

crystalline plates, and can be distilled between  $223^{\circ}$  and  $227^{\circ}$  under 195 mm. pressure. The aurochloride,  $C_8H_{17}NO_2, HCl, AuCl_3$ , crystallises in yellow needles sparingly soluble in water; the hydrobromide,  $C_8H_{17}NO_2, HBr$ , forms thick colourless tables.

*Diethylpropylglycoline*,  $C_7H_{17}NO_2$ , prepared from diethylamine and monochlorhydrin, is a thick colourless oil distilling at  $233-235^{\circ}$ . The platinochloride crystallises in reddish-yellow tables. By the action of benzoic chloride, a glycoleine is obtained; this in the free state forms a slightly coloured viscous liquid, and does not yield crystalline salts, with the exception of the picrate,  $C_{14}H_{21}NO_3 + C_6H_2(NO_2)_3.OH$ , in brilliant yellow plates.

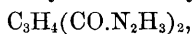
*Dimethylpropylglycoline*,  $C_5H_{13}NO_2$ , prepared from dimethylamine and monochlorhydrin, can be distilled unchanged at  $216-217^{\circ}$  as a colourless oily liquid. The platinochloride forms amorphous yellow flocks. By the action of benzoic chloride, two hydroxyl groups are replaced by benzoyl: the resulting glycoleine is best characterised by its picrate,  $C_5H_{11}NO_2(COPh)_2 + C_6H_2(NO_2)_3.OH$ , crystallising in yellow silky plates. The general formula of the compounds is—



( $R_2 = Me_2, Et_2$ , or the bivalent radical piperyl).

A. J. G.

**Acrolein-Carbamide.** By A. R. LEEDS (*Ber.*, **15**, 1159—1161).—H. Schiff has described a crystalline body, acryldiureide,



as formed by the action of acrolein on carbamide. The author entirely fails to confirm the existence of this substance, and finds that the product of the reaction is *acrolein-carbamide*,  $CO(NH)_2C_3H_4$ , a white amorphous substance sparingly soluble in alcohol, ether, chloroform, and carbon bisulphide; it is decomposed on heating.

A. J. G.

**Acrolein Carbamide.** By H. SCHIFF (*Ber.*, **15**, 1393—1397).—A reply to the criticisms of A. R. Leeds (*Ber.*, **15**, 1159) on the author's work on acrylureide (*Ann.*, **151**, 203).—A specimen of acrylureide, prepared by the action of acraldehyde on carbamide, has in the course of 14 years undergone a peculiar change, forming a yellow amorphous mass (acrylureide), and a white crystalline powder (acryldiureide).

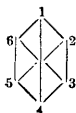
W. C. W.

**Allantoin and Asparagine in Young Leaves.** By E. SCHULZE and J. BARBIERI (*J. pr. Chem.* [2], **25**, 145—158).—The authors operated on birch, horse-chestnut, and plane trees. The branches covered with buds were cut from the trees in April, placed with their ends in water and so left, at the temperature of the room, until the sprouts arising from the buds showed no further growth, when they were removed from the branches and dried at a moderate heat.

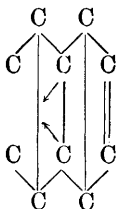
In all cases, asparagine was found in the extracts. Only a little asparagine was obtained from the chestnut, but leucine was detected. The young sprouts of the plane tree yielded allantoin to the extent of 0.5—1 per cent. on the dried leaves. Allantoin was also found, but in much smaller quantity, in young plane-leaves grown under normal conditions. No urea could, however, be detected. The authors can

therefore confirm J. Borodin (*Bot. Zeit.*, 1878, 802), with regard to the occurrence of asparagine in leaf-buds. F. L. T.

**Constitution of Benzene and Naphthalene.** By A. CLAUS (*Ber.*, 15, 1405—1411).—The objection which has been raised against the formula,



for the benzene nucleus, viz., that only two isomeric disubstitution products of benzene, can be represented by it, is groundless, since 1 : 4 does not correspond with 1 : 2 or 1 : 6. The author points out that the facts which are generally cited in support of the symmetrical formula for naphthalene, can be easily explained by the asymmetrical formula



This formula does not contain the benzene nucleus, but when either side of the naphthalene nucleus is split up by oxidation, the other side is capable of forming a benzene nucleus. W. C. W.

**Wroblewsky's Remarks on Benzene Formulæ.** By B. R. WARDER (*Ber.*, 15, 1411).

**Synthesis of Aromatic Hydrocarbons.** By H. GOLDSCHMIDT (*Ber.*, 15, 1425—1426).—When a mixture of isobutyl alcohol, zinc chloride, and benzene is rapidly heated to 300°, a fair yield of isobutyl benzene is obtained, but if the temperature of the mixture is slowly raised, a bad yield results. This is due to the fact that at temperatures below 300° the zinc chloride acts on the butyl alcohol, forming condensation products, whilst the benzene takes no part in the reaction. W. C. W.

**Oxidation of Substitution-products of Aromatic Hydrocarbons. Protection of a Group containing Two Carbon-atoms.** By I. REMSEN and W. A. NOYES (*Amer. Chem. J.*, 4, 197—205).—The experiments described in this paper were made with the view of ascertaining whether the protecting influence from oxidation by chromic acid which negative groups or atoms in the ortho-position relatively to methyl, have been shown to exert upon that radicle (see p. 186 of this volume), extends also to ethyl, propyl, and more complex residues. The authors experimented on para-diethylbenzene prepared by the action of sodium on a mixture of paradibromobenzene

and ethyl iodide. This hydrocarbon was converted into a sulphonic acid; the potassium salt of this acid by the action of phosphorus pentachloride into the corresponding sulphochloride; and this by the action of ammonia into the sulphonamide,  $\text{C}_6\text{H}_3\text{Et}(\text{SO}_2\text{NH}_2)\text{Et}$ , which when oxidised by chromic acid yielded the sulphamine-ethylbenzoic acid, represented by the formula  $\text{C}_6\text{H}_3\text{Et}(\text{SO}_2\text{NH}_2)\text{COOH}$ , showing that the ethyl-group next to the sulphamine-group was protected from oxidation, while the ethyl in the para-position relatively to the same negative group, was oxidised.

H. W.

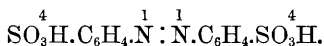
**Symmetrical Nitrotoluidine.** By H. BECKER (*Ber.*, **15**, 1138).—Symmetrical nitrotoluidine is readily obtained by the action of alcoholic ammonium sulphide on symmetrical dinitrotoluene. It forms yellowish-red needles, melting at  $95^\circ$ , readily soluble in hot water. The hydrochloride crystallises in large prisms. Benzoic chloride reacts violently within it, forming a crystalline benzoyl-derivative (m. p.  $177^\circ$ ).

A. J. G.

**Diphenylamine-Acraldehyde.** By A. R. LEEDS (*Ber.*, **15**, 1158—1159).—On gently heating diphenylamine with excess of acraldehyde, *diphenylamine-acraldehyde*,  $\text{C}_3\text{H}_4(\text{C}_{12}\text{H}_{10}\text{N})_2$ , is obtained as an amorphous red mass, readily soluble in chloroform, slightly soluble in alcohol and ethyl acetate; it does not crystallise from any of these solvents. It decomposes on heating. Dissolved in glacial acetic acid and treated with bromine, it gives a dark red precipitate, probably an addition-product.

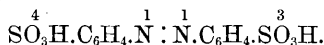
A. J. G.

**Azobenzenedisulphonic Acid.** By H. LIMPRICHT (*Ber.*, **15**, 1155—1156).—On heating  $\alpha$ -azobenzenedisulphonic acid with moderately concentrated hydrochloric acid for two hours at  $150^\circ$ , paramidobenzenedisulphonic acid (sulphanilic acid) is obtained in large quantity: so that the  $\alpha$ -acid has the constitution—



The substance obtained by reducing the  $\alpha$ -acid with stannous chloride and described (Abstr., 1882, 517) as  $\alpha$ -hydrazobenzenesulphonic acid, is sulphanilic acid.

$\beta$ -Azobenzenedisulphonic acid has the constitution



When heated at  $150^\circ$  with hydrochloric acid, it yields para- and meta-amidobenzenesulphonic acids, and it can be prepared by the oxidation of a mixture of equal molecules of para- and meta-amidobenzenesulphonic acids with potassium permanganate.

A. J. G.

*Note.*—On the constitution of azobenzenedisulphonic acids see also Janovsky (this vol., 835). Two different acids have been described as the  $\beta$ -disulphonic acid, that of Limpricht (this vol., 517) being an uncrystallisable syrup, and that of Janovsky (*loc. cit.*), a crystalline solid of the constitution  $\text{SO}_3\text{H}.\overset{3}{\text{C}_6\text{H}_4}.\overset{1}{\text{N}}:\overset{1}{\text{N}}.\overset{3}{\text{C}_6\text{H}_4}.\text{SO}_3\text{H}.$

**Dinitrobenzyl Alcohol.** By H. ORTH (*Ber.*, 15, 1136—1133).—The substance described under this name by Beilstein and Kuhlberg (*Annalen*, 147, 351) is shown to be *paranitrobenzyl nitrate*, as it is readily obtained by the action of silver nitrate on *paranitrobenzene*.

A. J. G.

**Nitrometacresols.** By H. ORTH (*Ber.*, 15, 1130—1132).—These substances are best prepared by the action of nitric acid on *cresol*, both being diluted with glacial acetic acid and strongly cooled; the resulting oil can be separated into two bodies by distillation in a current of steam. The volatile nitrometacresol [ $\text{OH} : \text{NO}_2 : \text{CH}_3 = 1 : 2 : 3$ , or  $1 : 6 : 3$  probably] crystallises in slender yellow needles (m. p.  $56^\circ$ ), and on precipitation with silver nitrate yields a red silver salt. The non-volatile nitrometacresol [ $\text{OH}_2 : \text{NO}_2 : \text{CH}_3 = 1 : 4 : 3$  ?] crystallises either in slender white needles or in long thick prisms of somewhat brownish colour (m. p.  $129^\circ$ ). The *potassium* derivative forms yellow plates, the *ammonium* salt long yellow needles, and the silver derivative is obtained as a yellow precipitate.

A. J. G.

**Nitroso- and Nitro-metacresol.** (Preliminary Notice.) By G. BERTONI (*Gazzetta*, 1882, 302—304).—The author prepares the nitroso-compound by the method recommended by Stenhouse and Groves for the preparation of the nitrosophenols, namely, by gradually adding to 1 part of metacresol cooled by a mixture of 30 pts. water and ice, a quantity of nitrosyl sulphate  $(\text{NO})\text{HSO}_4$ , rather greater than the calculated amount. Brown flocks then separate after a few seconds, and the reaction is completed in about half an hour. The product, separated by filtration, is quickly washed, then dried and purified by crystallisation from alcohol or benzene. The nitrosometacresol thus prepared is identical with that which Wurster and Riedel obtained from nitrosodimethyl-metatoluidine (*Abstr.*, 1880, 109).

The corresponding nitro-compound is easily obtained by adding an alkaline aqueous solution of potassium ferricyanide to an alkaline solution of the nitroso-compound, the mixture being kept at boiling heat, till the red-brown colour changes to yellow. The liquid after cooling is mixed with dilute sulphuric acid, and agitated with ether; the resulting ethereal solution is separated and freed from ether by distillation; and the nitro-compound is purified by repeated crystallisation from boiling water. It forms light yellow needle-shaped crystals, melting and turning brown at  $128^\circ$ , soluble in alcohol and in ether, and unites with the alkalis, forming well-defined salts, the sodium salt crystallising readily in tabular form.

From the well-known fact that all the monatomic phenols easily yield a single nitroso-derivative in which the NO-group occupies the para-position with regard to the methyl group, it follows that the nitroso-compound above described must have the constitution



the nitro-compound being similarly constituted.

H. W.

**Propyl-metacresol and its Derivatives.** By G. MAZZARA (*Gazzetta*, 1882, 333—336).—This phenol, as already stated by the

author (p. 838 of this volume), is obtained by the action of anhydrous magnesium chloride on a mixture of propyl alcohol and metacresol, 10 g. of the latter, 7 g. propyl alcohol, and 25 g. of the anhydrous chloride being heated for eight or ten hours in sealed tubes at 200—210°. The contents of the tubes are then treated with water and hydrochloric acid, and the oily layer, after being separated from the aqueous solution by a tap-funnel, is distilled. A small quantity of unaltered propyl alcohol and cresol then passes over below 100°, after which the temperature rises quickly to 210—250°, and a very dense oily liquid passes over, which is a mixture of propyl-*m*-cresol with its propylic ether; on treating this liquid with dilute potash, separating the resulting solution by a tap-funnel from the undissolved propylic ether, then agitating the solution with ether, and acidifying with hydrochloric acid, the new phenol is precipitated, and may be purified by rectification. Propyl-metacresol,  $\text{C}_6\text{H}_3(\text{C}_3\text{H}_7)(\overset{1}{\text{CH}_3})(\overset{3}{\text{OH}})$ , thus prepared is a slightly yellow liquid, boiling at 230—235°, under a pressure of 734 mm. It is soluble in alcohol and ether, slightly soluble in water. In a mixture of snow and salt it does not solidify, but becomes very thick. With ferric salts, it gives the coloration characteristic of the phenols.

*Propylic propylmetacresylate*,  $\text{C}_6\text{H}_3(\text{C}_3\text{H}_7)(\overset{1}{\text{CH}_3})(\overset{3}{\text{OC}_3\text{H}_7})$ , formed as above stated, is separated by treating the portions of the product boiling between 220° and 250° with dilute potash, which leaves the ether undissolved. When purified by repeated rectification, it forms a colourless liquid, boiling at 235—240°, lighter than water, having a slightly pungent odour, like that of oil of thyme. Heated in sealed tubes at 150° with hydriodic acid, it is decomposed, with formation of propyl iodide, a heavy liquid boiling at about 100°.

*Methylic propylmetacresylate*,  $\text{C}_6\text{H}_3(\text{C}_3\text{H}_7)(\overset{1}{\text{CH}_3})(\overset{3}{\text{OCH}_3})$ , is prepared by heating equivalent quantities of propyl-metacresol and potassium hydroxide dissolved in methyl alcohol, in a reflux apparatus placed in a water-bath. It is a yellowish fragrant liquid, boiling at about 226°.

*Propylmetacresyl acetate*,  $\text{C}_6\text{H}_3(\text{C}_3\text{H}_7)(\overset{1}{\text{CH}_3})(\overset{3}{\text{OC}_2\text{H}_3\text{O}})$ , is prepared by treating the phenol with acetic chloride, the action beginning at ordinary temperature, and being completed at the heat of a water-bath. The product purified by rectification is a liquid having a scarcely perceptible yellow colour, and faint acetic odour, boiling at 239—241°, and of the same density as water; decomposed by boiling potash-ley with reproduction of the phenol.

The *nitroso-derivative*,  $\text{C}_6\text{H}_2(\text{C}_3\text{H}_7)(\overset{1}{\text{CH}_3})(\overset{3}{\text{OH}})(\text{NO})$ , was prepared by pouring a potassic solution of 7 g. of the phenol in 1½ litres of water containing 30 g. potassium nitrite, and decomposing the mixture, well cooled with ice, with 30 g. acetic acid, mixed with 180 g. water, and cooled in like manner. A white precipitate is thereby obtained, which soon becomes coloured and resinous, but may be purified by separating it from the liquid, drying between paper, and washing with benzene, which removes the resinous substance, and dissolving it in hot benzene, from which it crystallises on cooling in small very light



yellow needles, which melt with decomposition at  $140^{\circ}$ , dissolve with moderate facility in alcohol and ether, very sparingly in water, and with reddish-yellow colour in aqueous potash.

H. W.

**Mesorcinol.** By E. KNECHT (*Ber.*, 15, 1375—1378).—Dinitromesitylene is reduced to *nitromesidine* by passing sulphuretted hydrogen through the hot alcoholic solution for two days, small quantities of ammonia being added from time to time. By the action of sodium nitrite on a solution of nitromesidine in dilute sulphuric acid, *nitromesitol* (hydroxynitromesitylene) is produced. Nitromesitol,  $C_9H_{11}NO_3$ , is deposited from a warm aqueous solution in yellow-coloured plates (m. p.  $64^{\circ}$ ), which are soluble in alcohol and ether. This compound is volatile in a current of steam. On reduction with tin and hydrochloric acid, amidomesitol is formed. The hydrochloride crystallises in colourless needles, which turn brown on exposure to the air.

*Mesorcinol*,  $C_6HMe_3(OH)_2$ , obtained by the action of sodium nitrite on an aqueous solution of amidomesitol hydrochloride, sublimes in white lustrous plates (m. p.  $149^{\circ}$ ; b. p.  $274^{\circ}$ ). The crystals are soluble in ether and in hot water. The solution reduces ammoniacal silver nitrate at the ordinary temperature. Ferric chloride produces a green coloration and a greyish precipitate. On distilling this mixture in a current of steam, Fittig's hydroxyisoxylquinone (*Annalen*, 180, 23) is obtained.

Fluorescent condensation-products are formed when mesorcinol is treated with warm sulphuric acid. A phthaleïn of mesorcinol has not yet been prepared.

W. C. W.

**Nitro-products of the Catechol Series.** By P. WESELSKY and R. BENEDIKT (*Monatsh. Chem.*, 3, 386—393).—A dilute ethereal solution of catechol (10 grams) is treated with red fuming nitric acid (4 c.c.), and after 24 hours the product is washed with water, separated, the ether distilled off, and the residue distilled with steam. In this way a *volatile mononitrocatechol* passes over; it crystallises from alcohol in long soft bright yellow needles melting at  $86^{\circ}$ , moderately soluble in water; the solution is coloured deep purple-red by potash, and then turns brown on standing in the air; barium hydroxide gives a red precipitate, which becomes blue with excess of the reagent. Concentrated nitric acid acts violently on nitrocatechol, with the formation of carbonic anhydride and oxalic acid. From the residue from the distillation with steam, a *non-volatile mononitrocatechol* can be separated by extraction with ether and crystallisation from xylene. It forms long yellowish needles melting at  $168^{\circ}$ .

Eugenol, prepared from oil of cloves by Wassermann's method (*Annalen*, 179, 369), is treated with nitric acid in a similar manner to that above described, and the excess of nitric acid precipitated from the product by the gradual addition of alcoholic potash; the supernatant liquid is then poured off from the potassium nitrate, and the nitroeugenol precipitated as potassium derivative by the further addition of alcoholic potash. The nitroeugenol is set free from the precipitate on the addition of dilute sulphuric acid, and is purified by crystallisation from boiling light petroleum. It forms large brilliant triclinic crystals

(melting at 43—44°), closely resembling potassium dichromate in appearance, sparingly soluble in water, easily in alcohol and ether. It can be distilled without decomposition, and is volatile with steam. With potash, it forms a salt with metallic lustre, which dissolves in water with an orange-red colour; with barium hydroxide, a flocky precipitate is formed. Nitric acid completely destroys nitro Eugenol. When nitro Eugenol is warmed with tin and hydrochloric acid, a violent reaction takes place, and *amidochlorhydroeugenol hydrochloride*,



is formed; it crystallises from water in white needles or leaflets; ammonia in small excess produces a pure white flocculent precipitate; with a large excess, the liquid becomes dirty violet. The precipitate dissolves in boiling water with partial decomposition; but crystallises from alcohol in a cluster of iridescent leaflets.

*Amidochlorhydroeugenol*,  $\text{C}_3\text{H}_6\text{Cl}.\text{C}_6\text{H}_2(\text{OMe})(\text{OH}).\text{NH}_2$ , melts at 97°, and can be distilled. Ammonia gives a transient yellow colour to the aqueous solution. The solution in dilute nitric acid gives no precipitate with silver nitrate until it is warmed, when silver chloride separates. When heated with acetic anhydride (2 pts.) and anhydrous sodium acetate ( $\frac{1}{2}$  pt.), nitro Eugenol is easily converted into *nitroaceteugenol*,  $\text{C}_3\text{H}_5.\text{C}_6\text{H}_2(\text{OMe})(\text{OAc}).\text{NO}_2$ , which crystallises from alcohol in clear glistening tablets (triclinic), melting at 61°. By the oxidation of nitroaceteugenol with permanganate at 70° (Tiemann's method, *Ber.*, 9, 418), a *nitrovanillic acid*,  $\text{C}_6\text{H}_2(\text{COOH})(\text{OMe})(\text{OH}).\text{NO}_2$ , is formed; it forms yellow needles melting at about 202°; above this point there is a crystalline sublimate, having the odour of vanilla: it dissolves in boiling water with a yellow colour, and crystallises out on cooling. The ammoniacal solution is deep orange-yellow. This nitrovanillic acid is apparently isomeric and not identical with Tiemann's (*Ber.*, 9, 148). From the nitration of pyrogallol, the authors have obtained only Barth's mononitropyrogallol.

D. A. L.

**Combination of Mono- and Bi-basic Acids of the Paraffin Series with Phenols.** By M. NENCKI (*J. pr. Chem.* [2], 25, 273—284).—The author follows up previous communications on this subject (*Abstr.*, 1881, 591, 811). As resaurin is produced by heating resorcinol and formic acid with zinc chloride, so is a substance obtained, having the properties of aurin, when phenol and formic acid are heated in presence of the same reagent; this substance is identical with the aurin obtained by heating phenol and oxalic acid with sulphuric acid. In like manner as phenol and resorcinol yield aurin and resaurin, so cresol, when treated in the same way, yields cresaaurin; to this the formula  $\text{C}_{22}\text{H}_{20}\text{O}_3$  has been given. Cresaaurin is a bright red amorphous powder, similar in properties to aurin, it dissolves readily in glacial acetic acid, forming a yellow solution; it is less soluble in alcohol and ether, and but sparingly in dilute acetic acid. It dissolves readily in solutions of the fixed alkalis to a magenta colour, passing to blue.

Orcinaurin is obtained by melting together one part of formic acid, one of anhydrous orcinol, and two of zinc chloride; when 20 grams

of orcinol are used, two hours' heating on the water-bath is sufficient for the reaction; the melt is thrown into water, which dissolves the zinc chloride and unattacked orcinol, the new product being left as an amorphous powder. It crystallises from glacial acetic acid in brownish-red needles, of the formula  $C_{22}H_{18}O_5$ . In order that this product should correspond with resaurin in the same manner as cresaurin corresponds with phenaurin, it should have the formula  $C_{22}H_{20}O_6$ . It is, therefore, deficient in one molecule of water—



Orcinaurin is easily soluble in ether, alcohol, and glacial acetic acid, insoluble in water; it possesses many of the properties of resaurin. When heated with glacial acetic acid and dry sodium acetate, it yields  $C_{22}H_{17}O_5\overline{Ac}$ , as a pale red amorphous powder. The attempt to obtain an acetyl derivative of resaurin was not successful.

The synthesis of aurin and its homologues offers a confirmation of the views of E. and O. Fischer, that aurin on the one hand and pararosaniline on the other are hydroxyl- or amido-derivatives of triphenylmethane (Abstr., 1879, 326, 384).

The behaviour of formic acid towards phenol when heated with zinc chloride is similar to that of the same acid towards aniline or guanidine.

Weith shows that Hofmann's methenyldiphenyldiamine is obtained by merely heating formic acid with aniline, and the heating of the salts of aniline or guanidine and formic acid with phenol in presence of a dehydrating agent, splits off the CH residue, and thus throws light on the formation of the aurins from formic acid and phenols.

J. F.

**Cholesterin.** By E. SCHULZE and J. BARBIERI (*J. pr. Chem.* [2], 25, 159—180).—The occurrence of cholesterin in plants has been observed firstly by Beneke (*Ann. Chem. Pharm.*, 122, 249), and subsequently confirmed by Hoppe-Seyler, Hesse, and others.

The authors, in examining the seeds and shoots of the yellow lupine (*Lupinus luteus*), found two varieties of cholesterin, the one in the cotyledons of the plant—and this modification they consider cannot distinctly be said to be a new one—the other in the shoots of the plant, showing different reactions from the other previously described cholesterins; this the authors propose to call caulosterin. The following numbers of the cholesterin group have now been described:—

	Melting point.	
1. Ordinary cholesterin.....	145—146°	} Lævorotatory.
2. Phytosterin (O. Hesse) ....	132—133	
3. Paracholesterin (Reinke and Rodewald) .....	134—134·5	
4. Caulosterin.....	158—159	
5. Isocholesterin.....	138—138·5	Dextrorotatory.

All these bodies, except ischolesterin, give the colour reaction with sulphuric acid and chloroform.

F. L. T.

**Nitrated Cresylethylic Oxides.** By E. KAYSER (*Ber.*, 15, 1132—1134).—The mononitrocresylethylic oxides are best prepared by treat-

ing the respective ethers with 2—6 parts of nitric acid, both ether and acid being diluted with its own volume of glacial acetic acid, and cooled to  $-10^{\circ}$  to  $-15^{\circ}$ . Any dinitroether formed at the same time can be removed by treatment with alcoholic ammonia, which, whilst converting the dinitro-compounds into dinitrotoluidines, is without action on the mononitro-bodies.

*Mononitro-orthocresylethylic oxide*,  $C_6H_3(NO_2)Me.OEt$  (m. p.  $71^{\circ}$ ), crystallises in long straw-yellow needles. Alcoholic ammonia at  $180-200^{\circ}$  is without action on it. Further nitration converts it into the dinitro-compound, melting at  $51^{\circ}$ . This latter on treatment with alcoholic ammonia is converted into *dimetanitro-orthotoluidine*, melting at  $208^{\circ}$ , whose constitution has been previously determined.

*Mononitrometacresyl ethyl oxide*, melting at  $54^{\circ}$ , crystallises from alcohol in colourless needles, and is not affected by alcoholic ammonia at  $100^{\circ}$ .

*Mononitroparacresylethylic oxide* [ $CH_3 : NO_2 : OEt = 1 : 3 : 4$ ] is liquid; it was also prepared by the action of ethyl bromide on the silver derivative of metanitroparacresol.

A. J. G.

**Amidocresylethylic Oxides.** By E. KAYSER (*Ber.*, 15, 1134—1136).—These are prepared from the corresponding nitro-ethers (see preceding abstract) by treatment with tin and hydrochloric acid. Their most important properties and derivatives are shown in the accompanying table:—

	<i>o</i> -Series.	<i>m</i> -Series.	<i>p</i> -Series.
Free base ....	Liquid .....	Liquid .....	M. p. $40-41^{\circ}$ . Crystallises in white needles, not readily soluble in water; does not crystallise well from ether, alcohol, or benzene.
Hydrochloride	$C_9H_{13}NO, HCl$ , silky plates.	Brilliant broad plates.	Fine silky needles.
Sulphate ....	$(C_9H_{13}NO)_2, H_2SO_4$ , readily soluble needles.	Large quadratic tables; effloresces readily.	Fine silky needles.
Nitrate .....	Slender needles, readily soluble.	.....	Satiny plates.
Oxalate .....	Silvery jagged plates.	Red tables.	—
Platinochloride	Clear yellow crystalline precipitate.	—	—
Aceto-com-pound	Crystallises from water in rhombic plates; from ether in large tables; from benzene in small cubes; m. p. $108^{\circ}$ .	Moderately soluble in hot water; crystallises in interlaced needles, m. p. $114^{\circ}$ .	Crystallises from water in brilliant white plates, apparently volatile with aqueous vapour; m. p. $106.5^{\circ}$ .

*Diamido-p-cresylethylic oxide* [ $OEt : NH_2 : CH_3 : NH_2 = 1 : 2 : 4 : 6$ ]  
4 l 2

is prepared by reduction of dinitro-paracresylethylic oxide (m. p. 75°); it is a colourless oily liquid of agreeable odour, and can be distilled unchanged. The hydrochloride,  $C_6H_2Me(NH_2)_2(OEt)_2HCl$ , crystallises in fine white silky needles, readily soluble in water.

A. J. G.

**Benzylmetacresylic Oxide.** By H. ORTH (*Ber.*, **15**, 1129—1130).—Benzylmetacresylic oxide prepared by the action of the potassium derivative of metacresol on benzyl chloride, melts at 43°, boils at 300—305°, crystallises in fine white plates, and is readily soluble in alcohol, ether, and benzene.

A. J. G.

**Sulphocinnamic Acids.** By CHASE PALMER (*Amer. Chem. J.*, **4**, 161—169).—Two of these acids are obtained by the action of fuming sulphuric acid on cinnamic acid at ordinary temperatures, the chief

product being the para-acid,  $SO_3H.C_6H_4.\overset{1}{CH} : \overset{4}{CH}.COOH$ , while the other is regarded by Rudnew (this Journal, 1875, p. 76) as the meta-acid, though from analogy the formation of the ortho-acid would appear more probable. The best yield of these acids is obtained by the use of sulphuric acid containing 20 per cent. of sulphuric anhydride. The two acids are most readily separated by converting them into barium salts, that of the para-acid being much the less soluble of the two.

By converting the barium salt of the para-acid into the corresponding potassium salt, and gently heating the latter with phosphorus pentachloride, *paracinnamic sulphochloride*,  $COCl.C_6H_4.C_2H_2.SO_2Cl$ , is obtained as a semi-fluid mass, which crystallises on cooling, and is converted by aqueous ammonia into the corresponding *sulphonamide*,  $CONH_2.C_6H_4.C_2H_2.SO_2NH_2$ . This amide, when purified by three or four crystallisations from hot water, forms clusters of needles easily soluble in hot, less in cold water, melting at 218°.

By oxidation with chromic acid mixture, this sulphonamide is converted into an acid,  $C_7H_7NSO_4 = SO_2NH_2.C_6H_4.COOH$ , the barium salt of which,  $C_7H_5BaNSO_4$ , is very soluble in water, and crystallises therefrom in granular aggregates.

*Parasulphamine-cinnamic acid,*



is formed by heating the amide just described with soda-ley as long as ammonia continues to be evolved. On neutralising the resulting solution with hydrochloric acid to throw down any undecomposed amide, and treating the filtered liquid with excess of hydrochloric acid, the sulphamine-cinnamic acid separates as a crystalline precipitate, and may be obtained by recrystallisation from boiling water in long needles. This acid is but slightly soluble even in hot water. Alcohol dissolves it readily, ether with difficulty. At 250°, it decomposes without melting. Its barium and calcium salts were obtained by neutralisation. The former crystallises in thick needles containing  $(C_9H_8SO_4N)_2Ba + 2H_2O$ ; the latter in clusters of slender needles containing  $(C_9H_8SO_4N)_2Ca + H_2O$ .

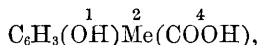
By oxidation with chromic acid mixture, parasulphamine-cinnamic

acid is converted into the acid  $C_7H_7NSO_4$ , likewise obtained, as above-mentioned, by oxidation of the sulphonamide.

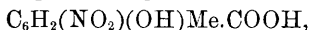
*Metasulphocinnamic acid* (?).—The barium salt contained in the solution from which the parasulphocinnamate had crystallised out was converted into a sulphonamide as above described for the para-compound, and this product was submitted to oxidation with potassium permanganate, but the results thereby obtained were not definite enough to lead to any satisfactory conclusion respecting the constitution of the acid. On fusing it with potassium hydroxide, no salicylic acid could be detected in the product, so that it does not appear to be the ortho-acid.

H. W.

**Derivatives of Parahydroxy-metatoluic Acid.** By R. W. MAHON (*Amer. Chem. J.*, **4**, 186—188).—This acid,

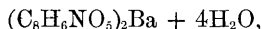


is most readily prepared by the method of Remsen and Iles, viz., by oxidising  $\alpha$ -xylenesulphonamide and fusing the resulting sulphamine-toluic acid with potassium hydroxide. It crystallises in long colourless needles having the composition  $2C_8H_7O_3 + H_2O$ , and melting at  $174.5^\circ$  (after drying at  $120^\circ$ ). By boiling it in quantities not exceeding a gram at a time, with strong nitric acid till it is completely dissolved, then immediately checking the action by copious addition of water and rapid cooling, a nitro-acid,



is obtained, which dissolves very freely in alcohol, especially when hot, yielding an intensely yellow solution, from which it separates in slender needles melting at  $86-87^\circ$ . It is very soluble also in ether, moderately soluble in water, and volatilises with steam.

*Calcium nitrohydroxytoluate*,  $[C_6H_2(NO_2)(OH)Me.COO]_2Ca.4H_2O$ , prepared by boiling the nitro-acid with finely powdered calspar, is soluble in water, yielding a deep red solution, from which it crystallises in groups of slender yellow needles, which give off their water, and acquire an orange-colour when heated. The anhydrous salt explodes at a higher temperature. The *barium salt*,



prepared in like manner, dissolves with red colour in water, and crystallises in stellate groups of slender orange-yellow needles. The anhydrous salt is crimson, somewhat hygroscopic, and explodes when heated.

The crystals of the nitro-acid, when heated in water, partly dissolve and are partly converted into a brownish-yellow oil having the same composition as the crystals, and melting, after solidification by cooling, at the same temperature. Both the oil and the crystals dissolve in ammonia, forming a red solution which contains the ammonium salt of the nitro-acid, gives off ammonia when treated with caustic soda, and yields a precipitate of the nitro-acid when treated with hydrochloric acid.

The *ammonium salt* crystallises from solution in arborescent groups

of fine yellow needles, changing to orange when exposed to moisture and exploding when heated. The sodium salt exhibits similar characters. The nitro-acid when precipitated by a stronger acid from the solution of one of its salts is pure white, but soon turns yellow. All the salts, as well as the acid itself, have great tinctorial power.

H. W.

**Decomposition of Tropine.** By A. LADENBURG (*Ber.*, **15**, 1140—1142; cf. *Ber.*, **15**, 1028).—The action of a large excess of bromine (5 mols.) on tropidine hydrobromide at a temperature of 165° yields dibromopyridine in large quantity. Its identity was proved by an exhaustive comparison of its properties with the dibromopyridine prepared from piperidine. As ethylene bromide is formed at the same time, it follows from these and the author's earlier results that tropidine is *ethylenehydromethylpyridine*,  $C_5H_6(C_2H_4)NMe$ .

A. J. G.

**Rotatory Power of Tyrosine and Cystine.** By J. MAUTHNER (*Monatsh. Chem.*, **3**, 343—347).—An examination of tyrosine yielded the following results with Wild's polaristrobometer in 2-decimeter tubes.

I. Solution in hydrochloric with 21.07 per weight of HCl; concentration = 4.51 grams to 100 c.c.; temperature = 16.20° C.  $\alpha = 0.72^\circ$ ,  $[\alpha]_D = -7.98^\circ$ .

II. Solution in potash with 11.598 per cent. weight KHO.

1. Conc. = 5.80,  $t = 20.5^\circ$  C.,  $\alpha = -1.045^\circ$ ,  $[\alpha]_D = -9.01^\circ$ .

2. Conc. = 11.51,  $t = 16.1^\circ$  C.,  $\alpha = -2.040^\circ$ ,  $[\alpha]_D = -8.86^\circ$ .

Cystine is strongly lævorotatory.

D. A. L.

**Cystine.** By E. KÜLZ (*Ber.*, **15**, 1401).—Cystine deviates the ray of polarised light 142° to the left. It is therefore, optically twice as powerful as grape-sugar.

W. C. W.

**Derivatives and Constitution of Opianic and Hemipinic Acid.** By R. WEGSCHEIDER (*Monatsh. Chem.*, **3**, 348—380).—From previous work on this subject it was a matter of conjecture whether the carboxyl-groups are ortho or para to one another; the author has undertaken the solution of this problem.

*Potassium opianate*,  $C_{10}H_9KO_5$ , crystallises either in granules or short prisms with  $3\frac{1}{2}$  mols.  $H_2O$ , or in thin brittle leaflets or thick long white prisms, with  $2\frac{1}{2}$  mols.  $H_2O$ , or in large feebly yellow rhombic plates with 1 mol.  $H_2O$ ; the water of crystallisation is driven off at 100° in each case. This salt is soluble in water and alcohol, only sparingly in absolute alcohol. *Silver opianate* is best prepared by precipitating a solution of potassium opianate with silver fluoride; it is at first precipitated in hemispherical groups of small prisms, but usually forms a magma of white prisms, which turn yellow on exposure to light. *Methyl opianate* is made by shaking together silver opianate, methyl alcohol, and methyl iodide (theoretical quantity), and leaving the mixture for some time. It crystallises from methyl

alcohol in large hexagonal plates, or in tufts of needles; from alcohol in long flat obliquely cut needles; from ether in thick four-sided tables or very short, thick, oblique prisms. It is easily soluble in most ordinary solvents, except water, in which it is but sparingly soluble. It softens at  $63^{\circ}$ , melts at  $83-85^{\circ}$ , and remains fused for some time even at the ordinary temperature. When carefully heated it partially sublimes. It is easily saponified by potash, or by prolonged boiling with water. If methyl opianate is very carefully oxidised with aqueous permanganate, it is partially converted into an *acid methyl hemipinate*. This the author designates as the  $\alpha$ -acid methyl hemipinate; it is moderately soluble in water, and crystallises from it in long, narrow, flat, brittle, glistening needles (m. p. in water of crystallisation  $96-98^{\circ}$ ; dry substance,  $121-122^{\circ}$ ), easily soluble in most ordinary solvents, sparingly in carbon bisulphide, and almost insoluble in light petroleum. The aqueous solution gives a pale yellow-brown precipitate with ferric chloride, and decomposes potassium carbonate with evolution of carbonic anhydride. *Sodium methyl hemipinate* forms white crystals, which decompose at  $200^{\circ}$ . Its solution precipitates ferric chloride, silver nitrate, and lead acetate, in the last case the precipitate is soluble in excess of the reagent. This ethereal salt saponifies with potash, yielding hemipinic acid. By passing a current of hydrochloric acid gas through a methyl alcohol solution of hemipinic acid, and warming, the author has prepared another  $\beta$ -acid methyl hemipinate (m. p.  $137-138^{\circ}$ ), which is easily soluble in water, other solubilities like the  $\alpha$ -derivative. It crystallises from acetic acid in moss-like masses, from ethyl alcohol and benzene in ramifications of ill-formed needles, from alcohol in stellate groups of prisms, and from benzene in plates. It contains no water of crystallisation, and gives no precipitate with ferric chloride. There are therefore two isomeric acid methyl hemipinates, and hemipinic acid can be thus represented,  $C_6H_2(OMe)_2(COOH)_2$  [ $COOH : COOH = 1 : 2$ ]; opianic acid,  $COH.C_6H_2(OMe)_2COOH$  [ $COH : COOH = 1 : 2$ ];  $\alpha$ -acid methyl hemipinate,



$1 : 2 : 3 : 4$ ];  $\beta$ -acid methyl hemipinate, [ $COOMe : COOH : Me : Me = 1 : 2 : 3 : 4$ ].

When heated, both acid methyl hemipinates yield hemipinic anhydride. Hemipinic anhydride is easily soluble in most solvents, moderately in ether, sparingly in carbon bisulphide, and not at all in light petroleum; it generally crystallises in needles.

By distilling the  $\alpha$ -ethereal salt with lime, the author obtains a mixed product, from which he isolates *methyl* [ $3 : 4$ ] *dimethoxybenzoate* (m.p.  $164-165^{\circ}$ ); *guaiacol*, recognised by odour and by ferric chloride lead acetate, and ammoniacal silver nitrate reactions; *methylnorhemipinic acid*, melting at  $153-155^{\circ}$  with evolution of gas, very soluble in water, sparingly in ether; violet coloration with ferric chloride; *isovanillic acid*, needles melting at  $236-238^{\circ}$ , easily soluble in ether, sparingly in water. By the action of strong hydrochloric acid,  $\alpha$ -acid methyl hemipinate is decomposed, passing through the following stages (all these substances have been identified); hemipinic acid,



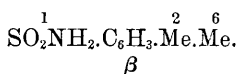
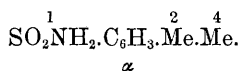
methylnorhemipinic acid,  $C_6H_2(COOH)_2(OMe).OH$  [ $OH : OMe = 3 : 4$ ], isovanillic acid,  $C_8H_2(COOH)(OH).OMe$  [ $1 : 3 : 4$ ], and (3:4)-dihydroxybenzoic acid. The author has tried the decomposition of hemipinic acid with hydriodic acid, and obtained results analogous to those of Wright and Beckett.

D. A. L.

**Ethyllic Benzylchloromalonate.** By C. A. BISCHOFF and A. EMMERT (*Ber.*, **15**, 1112—1114).—By the action of cold alcoholic ammonia on ethyllic benzylchloromalonate, *benzylchloromalonamide* is formed; it crystallises in white needles united in nodular masses, is soluble in alcohol, melts at  $80^\circ$ , turns brown at  $180^\circ$ , and is decomposed at  $210$ — $220^\circ$ .

A. J. G.

**Benzoyl-derivatives of the Xylenesulphonamides.** By R. W. MAHON (*Amer. Chem. J.*, **4**, 192—197).—The investigations of Remsen and Iles (*Amer. Chem. J.*, **i**, 33), and of Jacobsen (*Ber.*, 1877, 1009), have shown that the  $\alpha$ - and  $\beta$ -sulphonamides obtained from metaxylene have the following formulæ:—



In the  $\beta$ -amide therefore, both the methyl-groups are in the ortho-position with respect to the group  $SO_2NH_2$ . Now Remsen has shown in numerous instances that in such a position the methyl-groups are protected from the action of oxidising agents, whereas in the meta- and para-positions they are attacked and oxidised to  $COOH$ . According to Jacobsen however (*Ber.*, **11**, 891), this  $\beta$ -amide conducts itself just like the  $\alpha$ -amide, being converted by chromic acid into a monobasic acid. It seemed therefore desirable to obtain a considerable quantity of the pure  $\beta$ -sulphonamide, in order to make an exact study of its behaviour under the influence of oxidising agents. Its direct separation from the  $\alpha$ -amide being extremely difficult, the author endeavoured to effect the separation by first converting the mixed amides into their benzoyl-derivatives, which it was hoped would exhibit more decided acid properties (as found by Anna Wolkow in the case of the benzoyl-derivatives of the toluenesulphonamides), and so might yield salts separable by crystallisation.

For this purpose the mixed sulphonamides were heated with benzoic chloride at  $150$ — $160^\circ$  in an oil-bath till gas ceased to be given off, the black cakes left in the flask were dissolved in hot alcohol, and the product was recrystallised from water and alcohol, whereby it was obtained in short colourless needles melting at  $149$ — $151^\circ$ . This recrystallised product when heated with alcoholic potash yielded the simple  $\alpha$ -xylene-sulphonamide. It also dissolved easily in ammonia, and the ammoniacal solution, after being freed from excess of ammonia, gave with barium chloride a white crystalline precipitate of barium  $\alpha$ -benzoylxylene-sulphonamide,  $(C_6H_3Me_2.SO_2NBz)_2Ba$ , which separates from solution in slender colourless needles, sparingly soluble in water. The calcium salt,  $(C_6H_3Me_2.SO_2NBz)_2Ca + H_2O$ , prepared by boiling the

acid with pulverised calcspar, crystallises in slender needles, soluble in alcohol and ether, sparingly soluble in water.

When mixtures of the  $\alpha$ - and  $\beta$ -xylenesulphonamide (containing a large proportion of the latter) were heated with benzoic chloride, a product was obtained, the ammoniacal solution of which yielded, on addition of hydrochloric acid, a gummy mass, from which by repeated crystallisation from alcohol, several crops of  $\alpha$ -benzoylxylenesulphonamide were obtained; and after the removal of these, and subsequent evaporation to near dryness, an oily substance separated, which solidified to a clear brownish-yellow gum still holding in suspension crystals of the  $\alpha$ -benzoylamide. This oily substance dissolved easily in ammonia and in alkaline carbonates, and was reprecipitated therefrom by hydrochloric acid; when boiled in water with carbonate of barium or calcium, it yielded solutions from which hydrochloric acid reprecipitated the original oil, leaving a solution containing barium or calcium. From these reactions, it may be inferred that the oily substance consisted mainly of  $\beta$ -benzoylxylenesulphonamide; but it was not obtained pure enough to yield definite results. H. W.

**Action of Dichlorethyl Oxide on Benzene in Presence of Aluminium Chloride.** By E. WAAS (*Ber.*, 15, 1128—1129).—This reaction yields diphenylethane and triphenylethane,  $C_{20}H_{18}$ , a red oil with violet fluorescence boiling above  $360^\circ$ , and readily soluble in ether. The course of the reaction was experimentally shown to be as follows: the aluminium chloride first converts the dichlorethyl oxide into monochloraldehyde, which, reacting with the benzene, forms first monochlorodiphenylethane, and finally triphenylethane.

A. J. G.

**Carbostyryl.** Part III. By P. FRIEDLÄNDER and A. WEINBERG (*Ber.*, 15, 1421—1426).—Good yields of ethylcarbostyryl are obtained by the action of sodium ethylate on monochloroquinoline, or by the action of ethyl iodide on carbostyryl silver,  $C_9H_6NOAg$ . Attempts to prepare ethylcarbostyryl from ethyl amidocinnamate or ethylamidocinnamic acid were unsuccessful.

*Ethyl orthamidocinnamate* is formed when a hot alcoholic solution of ethyl nitrocinnamate is reduced with tin and hydrochloric acid. After removing the tin from the crude product by means of sulphuretted hydrogen, the ethereal salt is precipitated in pale yellow needles (m. p.  $77^\circ$ ) by the addition of sodium acetate. The crystals dissolve freely in the usual solvents, forming yellow solutions, which exhibit a greenish-yellow fluorescence. The hydrochloride is sparingly soluble in hydrochloric acid. The neutral solution turns yellow when heated, owing to partial dissociation; on cooling, the solution again becomes colourless. The acetic derivative is deposited from its alcoholic solution in white needles (m. p.  $137^\circ$ ). Ethyl amidocinnamate is decomposed by hydrochloric acid at  $120^\circ$ , carbostyryl being formed.

When a cold alcoholic solution of ethyl nitrocinnamate is treated with zinc-dust and hydrochloric acid, hydrocarbostyryl (m. p.  $163^\circ$ ) is produced.

Ethylcarbostyryl is not readily attacked by acid reducing agents. By sodium amalgam, in the cold, it is converted into dihydroethyl-

carbostyryl, but if a hot solution is used, then in addition to dihydroethylcarbostyryl an unstable ethereal salt of hydrocarbostyryl and a small quantity of an oily liquid, probably tetrahydroethylcarbostyryl, are produced.

When bromine-vapour acts on ethylcarbostyryl, monobromomethylcarbostyryl is formed together with other products. This bromo-derivative crystallises in white needles melting at 93°. It is decomposed by hydrochloric acid, yielding methyl chloride and bromocarbostyryl melting at 266°.

Bromine-water acts on carbostyryl, forming mono- and dibromo-substitution products. Dichlorocarbostyryl, prepared by boiling a solution of carbostyryl in acetic and hydrochloric acids with potassium chlorate, crystallises in white needles melting at 249°. It is converted into trichloroquinoline,  $C_9H_4Cl_3N$ , by the action of phosphorus pentachloride. This body is deposited from alcohol in needle-shaped crystals which melt at 160·5°. It is soluble in strong hydrochloric acid, but is reprecipitated on the addition of water to the solution.

W. C. W.

**Synthetical Amylnaphthalene.** By T. LEONE (*Gazzetta*, **12**, 209—211).—By the action of phosphorus and hydriodic acid on lapachic acid, Paternò obtained a hydrocarbon (b. p. 304—306°), which he considered to be amylnaphthalene. For the sake of comparison, the author has prepared amylnaphthalene synthetically by acting on a mixture of  $\alpha$ -monobromonaphthalene, amyl bromide, and ether with metallic sodium. The action is most energetic at first, but when it becomes quieter the mixture is boiled for several hours, the ether distilled off, and the residue submitted to fractional distillation. The portion passing over between 290° and 315°, after repeated distillation over sodium, yields amylnaphthalene boiling at 303°. The picric acid compound prepared from this is of a fine yellow colour, and melts at 85—90°, whilst the corresponding compound of amylnaphthalene from lapachic acid forms deep orange-red crystals, melting at 140—141°. From this it would seem that the two hydrocarbons are isomeric and not identical, notwithstanding the boiling points are the same.

Paternò's researches render it probable that the amyl in his amylnaphthalene from lapachic acid has the constitution  $—CH_2.CH_2.CHMe_2$ , that is, the same as in fermentation amyl alcohol, so that the isomerism of the two hydrocarbons would seem to be due to the position of the amyl group; the synthetical amylnaphthalene being the  $\alpha$ -compound, whilst Paternò's, as he originally suggested, is the  $\beta$ -compound.

C. E. G.

**Oxidation of Pentachloronaphthalene.** By A. CLAUS and L. SPRUCK (*Ber.*, **15**, 1401—1405).—Tetrachlorophthalic acid, but not a trace of monochlorophthalic acid, is formed by the oxidation of pentachloronaphthalene by nitric acid. Hence Wreden's statement (*Ber.*, **2**, 591) that the formation of tetrachlorophthalic acid is due to a secondary, and not to a primary reaction is improbable. Tetrachlorophthalic acid is reduced to phthalic acid by the action of sodium amalgam on its alcoholic solution.

*Trichloronaphthaquinone*,  $C_{10}H_3Cl_3O_2$ , is produced when pentachloronaphthalene is boiled with fuming nitric acid until chlorine is no longer evolved (about 30 hours). This substance crystallises in yellow needles (m. p.  $250^\circ$ ), soluble in hot alcohol. By the addition of water to the hot alcoholic solution, colourless plates (m. p.  $95^\circ$ ) can be obtained.

Trichloronaphthaquinone dissolves in alcoholic soda, yielding a red liquid, from which hydrochloric acid throws down a colourless crystalline precipitate (m. p.  $250^\circ$ ).  
W. C. W.

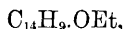
**Action of Chloroform on  $\beta$ -Naphthol.** By G. ROUSSEAU (*Compt. rend.*, **95**, 39—41).—The products of the action of chloroform on  $\beta$ -naphthol are (1) the glycol,  $C_{22}H_{14}O_2$ , previously described (*Compt. rend.*, **94**, 133), (2) the aldehyde,  $C_{11}H_8O_2$ , which has been investigated by Kauffmann (*Ber.*, **15**, 808), (3) a brown resin, soluble in alkalis, which always accompanies the aldehyde and may be freed from the latter by treatment with light petroleum, in which the aldehyde alone dissolves. Thus purified the resin contains 47 per cent. of carbon. (4) The glycollic ether,  $C_{22}H_{12}O$ , previously described, (5) a resin insoluble in alkalis, but soluble in alcohol, which contains 96 per cent. of carbon, and consists mainly of condensed hydrocarbons. In all cases, carbonic oxide is given off, and under certain conditions in neutral solution, a monhydric alcohol,  $C_{22}H_{14}O$ , is formed in small quantity. The resin soluble in alkalis is probably formed by the oxidation of the aldehyde, whilst a portion of the latter undergoes hydrogenation and condenses, with elimination of water, to form the glycol. The most important feature of the reaction is the conversion of a phenol into a compound having an alcoholic function. Holdmann has prepared  $\beta$ -naphthylamine by heating  $\beta$ -naphthol in a current of ammonia gas, and Graebe has obtained the ethers of the naphthols by boiling the latter with dilute sulphuric acid. It would appear therefore that the naphthols are less stable than the phenols and more analogous to the alcohols. The formation of the glycol may be thus explained. 2 mols. of the aldehyde, under the influence of the hydrogenation previously referred to, lose their hydroxyl in the form of water, and unite to form a di-naphthyl group. The two  $-COH$  groups, both probably in the ortho-position with respect to the point of union, undergo a molecular transformation, and are converted into the groups  $\equiv C.OH$  characteristic of tertiary alcohols. It follows that the new glycol is a non-saturated tertiary glycol, and has the constitution



**Aromatic Ethers.** By H. v. NIEDERHAUSEN (*Ber.*, **15**, 1119—1125).—Calcium phenol, on dry distillation, yields diphenylene oxide and a little benzene. Calcium  $\alpha$ -naphthol yields naphthalene and  $\alpha$ -dinaphthalene oxide. Calcium  $\beta$ -naphthol gives naphthalene,  $\beta$ -dinaphthalene oxide, and a substance,  $C_{21}H_{14}O$  (m. p.  $300-305^\circ$ ), crystallising in colourless needles or nacreous plates, which cannot be

volatilised without partial decomposition. Sodium phenol and sodium metaphosphate, when distilled together, yield much diphenyl ether, and a small quantity of methylenediphenyl ether. A. J. G.

**Naphthol and Anthrol Ethers.** By C. LIEBERMANN and A. HAGEN (*Ber.*, 15, 1427—1430).—The properties of *anthrolethylic ether*,



have been previously described (*Ber.*, 12, 589). This substance is easily prepared by boiling a concentrated alcoholic solution of anthrol with half its volume of hydrochloric acid (20 per cent.): the crystalline mass which is deposited when the mixture cools is washed with soda solution in order to remove unaltered anthrol. The pure ether melts at  $145^\circ$ .

*Anthrolmethylylic ether*,  $\text{C}_{14}\text{H}_9.\text{OMe}$ , melts at  $175$ — $178^\circ$ , and resembles the preceding compound in its properties.

$\alpha$ - and  $\beta$ -*naphthoethylylic ethers*, previously described by Schäffer (*Ann.*, 152, 287), can be prepared by heating at  $150^\circ$  in sealed tubes for seven hours, a mixture of naphthol (1 part), alcohol (3), and hydrochloric acid (1 part). Etherification takes place more easily with  $\beta$ - than with  $\alpha$ -naphthol.

*Diethoxynaphthalene*,  $\text{C}_{10}\text{H}_6(\text{OEt})_2$ , crystallises in nacreous plates (m. p.  $104^\circ$ ). Attempts to prepare ethers by the action of hydrochloric acid and alcohol on phenol, resorcinol, quinol, pyrogallol, and orthonitrophenol, were unsuccessful.

On the addition of strong nitric acid to a concentrated solution of anthrolethylic ether in glacial acetic acid, dinitranthrolethylic ether,  $\text{C}_{14}\text{H}_7(\text{NO}_2)_2.\text{OEt}$ , is deposited in needle-shaped crystals. An analogous compound has also been obtained from anthrolmethylylic ether.

W. C. W.

**Naphthalene-derivatives.** By F. GRAEFF (*Ber.*, 15, 1125—1127; cf. *Abstr.*, 1881, 822).—Mononitronaphthoic acid (m. p.  $235^\circ$ ), when oxidised with an alkaline permanganate solution, yields mainly an acid agreeing in its properties with the nitro-phthalic acid melting at  $212$ — $220^\circ$ , in which the carboxyl- and nitro-groups have the 1 : 2 : 3 positions. From this it follows that the nitro-group in nitronaphthoic acid is in the  $\alpha$ -position, and is not attached to the same  $\text{C}_4\text{H}_4$  nucleus as the  $\text{COOH}$ -group. As it has been shown by Eckstrand that the latter also occupies an  $\alpha$ -position, mononitro-naphthoic acid must have the constitution  $[\text{NO}_2 : \text{COOH} = 1 : 1']$  or  $[\text{NO}_2 : \text{COOH} = 1 : 3']$ , but there is at present no evidence to show which.

A. J. G.

**Products of the Decomposition of Mixed Aromatic Thiocarbamides by Acids.** By K. MAINZER (*Ber.*, 15, 1412—1421).—*Phenyl- $\alpha$ -naphthylthiocarbamide* (m. p.  $158^\circ$ ) is decomposed by strong hydrochloric acid at  $150^\circ$  into phenylthiocarbamide,  $\alpha$ -naphthylthiocarbimide, phenylamine, and  $\alpha$ -naphthylamine.

*Orthotolyl- $\alpha$ -naphthylthiocarbamide* is deposited as a white crystalline mass on warming an alcoholic solution of  $\alpha$ -naphthylthiocarbimide and orthotoluidine, or of orthotolylthiocarbimide and  $\alpha$ -naphthylamine.

It is decomposed at 150° by hydrochloric acid, forming  $\alpha$ -tolyl- and  $\alpha$ -naphthyl-thiocarbimide, and orthotoluidine and  $\alpha$ -naphthylamine.

*Paratolyl- $\alpha$ -naphthylthiocarbimide*, prepared by warming an alcoholic solution of paratolylthiocarbimide (m. p. 26°, b. p. 238°) and  $\alpha$ -naphthylamine, crystallises in white needles melting at 168°. By heating it with strong hydrochloric acid this substance is decomposed into paratolyl- and  $\alpha$ -naphthyl-thiocarbimide, and paratoluidine and  $\alpha$ -naphthylamine.

*Phenyl- $\beta$ -naphthylthiocarbimide* crystallises in plates melting at 155—157°. By repeated recrystallisation from boiling alcohol, this substance appears to undergo decomposition, as the melting point rises without becoming constant. When this substance is heated with hydrochloric acid at 104°, it splits up into phenylthiocarbimide,  $\beta$ -naphthylthiocarbimide,  $\beta$ -naphthylamine, and aniline.

*Orthotolyl- $\beta$ -naphthylthiocarbimide* (m. p. 194°) is decomposed by hydrochloric acid at 150° into orthotolyl- and  $\beta$ -naphthyl-thiocarbimides, orthotoluidine, and  $\beta$ -naphthylamine.

*Paratolyl- $\beta$ -naphthylthiocarbimide* (m. p. 164°), under similar treatment, yields analogous decomposition products.

When *phenylorthotolylthiocarbimide* is decomposed by hydrochloric acid, phenyl- and orthotolyl-thiocarbimides are produced.

From the above reactions, it appears that mixed aromatic thiocarbimides, on decomposition by hydrochloric acid, yield two thiocarbimides and two amines.

W. C. W.

**Action of Cyanogen on Sodium-menthol.** By G. ARTH (*Compt. rend.*, **94**, 872—873).—Dry cyanogen is absorbed by a solution of sodium-menthol in dry toluene, the mixture gradually becoming pasty. When cold, it is washed with water, and the hydrocarbon distilled off: the residue is a crystalline mass, which separates from boiling alcohol in slender prismatic needles with rhomboidal base, soluble in the usual solvents. It sublimes easily at 100°, melts at 165°, and decomposes at about 200°, yielding cyanuric acid. It has the composition and properties of menthol-urethane,  $C_{11}H_{21}NO_2$ , being decomposed by alcoholic potash with formation of potassium cyanate.

The alcoholic mother-liquors from which the menthol-urethane has been crystallised, deposit a viscous mass on evaporation: this, when boiled for a long time with water, gives off menthol and ammonia, and on cooling solidifies to a crystalline cake soluble in boiling alcohol. It melts at 105°, and was proved to be menthol carbonate analogous to Haller's borneol carbonate (this vol., 528).

C. E. G.

**Campholurethane.** By A. HALLER (*Compt. rend.*, **94**, 869—871).—The author, under the name of *borneol cyanate* (*ibid.*, **92**, 1511), has described a compound which is obtained along with cyanocamphor by the action of cyanogen or cyanogen chloride on sodium-camphol, but he now finds that it is really campholurethane. Like the urethanes, it combines with aldehydes, the compounds with benzaldehyde being formed on passing hydrochloric acid gas into an ethereal solution of the two substances, and allowing the ether to evaporate spontaneously. The benzaldehyde compound,  $CHPh(NH.COOC_{10}H_{17})_2$ ,

crystallises in silky needles melting at 185—187°, only sparingly soluble in cold alcohol or ether, but soluble in chloroform, benzene, &c. It is decomposed by boiling with water, and more rapidly with dilute hydrochloric acid, giving off an odour of benzaldehyde. The corresponding compound formed with ethaldehyde is viscous, and cannot be distilled without decomposition.

When campholurethane is heated at 140° with excess of acetic anhydride, it is decomposed with evolution of carbonic anhydride and formation of acetamide and borneol acetate as follows:



This mode of decomposition is identical with that observed by M'Creath in the case of ethylurethane.

Although these reactions are those of a urethane, it differs in some of its properties from the ethereal carbonates, which is perhaps due to its high molecular weight or to the secondary nature of campholic alcohol.

C. E. G.

**Conversion of Pyrroline into Pyridine.** By G. L. CIAMICIAN and M. DENNSTEDT (*Ber.*, 15, 1172—1181).—The authors have previously (Abstr., 1881, 826) obtained by the action of chloroform on pyrroline, a compound which appeared to be a chloropyridine, but as they were unable to remove the chlorine from the product, they were unable to speak with certainty as to its nature. They have now investigated the action of bromoform on pyrroline, and find the compound produced to be identical with the bromopyridine which Hofmann obtained (Abstr., 1879, 734) by the direct action of bromine on pyridine.

*Monobromopyridine* is a liquid of strongly alkaline reaction, it boils at 169.5° under a pressure of 760.5 mm., and has sp. gr. of 1.645 at 0°. Monobromopyridine hydrochloride can be obtained in deliquescent needles. The platinochloride ( $\text{C}_5\text{H}_4\text{BrN}.\text{HCl}$ )<sub>2</sub>.PtCl<sub>4</sub> + 2H<sub>2</sub>O, crystallises in honey-yellow prisms belonging to the monoclinic system—

$$a : b : c = 1.20735 : 1 : 1.18815.$$

Observed forms 110, 101, 001,  $\bar{1}01$ ,  $\bar{3}02$ , 011.

On treatment with bromine at 230—250°, monobromopyridine is converted into Hofmann's dibromopyridine.

Carbon tetrachloride acting on potassium-pyrroline also converts it into monochloropyridine, from which it would seem that the chlorine-atom is attached to that carbon-atom which has newly entered the pyridine molecule.

Bromopyridine, unlike chloropyridine, is easily reduced by nascent hydrogen, a mixture of pyridine and dihydropyridine being obtained.

A. J. G.

**Action of Nascent Hydrogen on Pyrroline.** By G. L. CIAMICIAN and M. DENNSTEDT (*Gazzetta*, 1882, 290—292).—When a solution of pyrroline in excess of acetic acid (sp. gr. 1.06) is gently heated for three or four days in a reflux apparatus with zinc-dust, fresh quantities of which are added as it dissolves, the liquid on cooling acquires a deep green colour, and solidifies to a mass of crystals: by dissolving these on water, and distilling the solution in a current of steam,

the basic product of the reaction may be separated from unaltered pyrroline. The solution thus obtained is treated, after sufficient dilution, with hydrogen sulphide to separate the zinc, and the filtered liquid is concentrated, with addition of a little hydrochloric acid, whereby any remaining portions of pyrroline are resinified during the evaporation. The concentrated solution is then treated with a large excess of solid potash and distilled with steam; the alkaline distillate is saturated with hydrochloric acid and evaporated to dryness; the crystalline residue is boiled with hydrochloric acid to destroy the last traces of pyrroline; the acid is evaporated off; the residue dissolved in water, with addition of a large excess of potash; and the oily base thereby separated is distilled with steam, the first portion of the distillate, which contains nearly the whole of the base, being collected apart and treated with solid potash, and the base which then again separates in the form of an oil, being further dried by prolonged contact with fused potash and redistilled: it then passes over completely between  $90^{\circ}$  and  $91^{\circ}$ .

The base thus obtained is a colourless liquid having a strongly alkaline reaction and ammoniacal odour; it is extremely soluble in water, and absorbs moisture from the air, fuming strongly in contact therewith. Its composition has been determined by the analysis of its platinumchloride  $(C_4H_7N, HCl)_2PtCl_4$ , which dissolves in boiling water, and separates on cooling in large orange-yellow anhydrous crystals.

The formula  $C_4H_7N$  is that of a dehydrogenised pyrroline, and it is probable that, in the formation of the new base, the  $NH$ -group of pyrroline is converted into an  $NH_2$ -group, inasmuch as this base gives with chloroform the reactions of the carbylamines. H. W.

**Action of Bromine on Quinoline and Pyridine.** By E. GRIMAUX (*Compt. rend.*, 95, 85—87).—Two parts of bromine are added to a well-cooled mixture of 1 part quinoline with 1 to 3 parts of water, and the red product which separates out is dissolved in chloroform at a gentle heat. The slender red needles which separate out on cooling are very unstable, and lose bromine and hydrobromic acid when exposed to the air. The ratio of carbon to bromine is  $C_9$  to  $Br_4$ , and the formula of the compound is therefore  $C_9H_7NBr_4$ . On treatment with potash or hydrogen sulphide, it yields the original quinoline. If the chloroform solution is *boiled* for five or six minutes, and then left at rest, hard bulky red-brown crystals of *hydrobromide of quinoline bromide* are deposited after 24 hours. The same compound is obtained by moistening the crude bromide with its own weight of alcohol. After some time, heat is developed, the liquid boils, and the bromide dissolves. On cooling, large red crystals of the hydrobromide are deposited, and the odour of bromal is perceived. *Hydrobromide of quinoline bromide*,  $C_9H_7N, Br_4, HBr$ , forms large red anhydrous prisms melting at  $86^{\circ}$ , very soluble in alcohol and ether, slightly soluble in hydrobromic acid, insoluble in water and chloroform. When heated with water, it is converted into quinoline hydrobromide, and the same change is effected by hydrogen sulphide. When treated with ammonia, it is decomposed with evolution of nitrogen. It dissolves in potash and in sodium carbonate, and hydro-



bromic acid precipitates from the solution a yellow powder having the same melting point as the original substance. By prolonged treatment with potash, it is converted into quinoline.

Pyridine under the same conditions also combines directly with bromine to form a still more unstable compound, which crystallises in long needles, and may be isolated by dissolving the crude product in cold chloroform, and then placing the solution in a freezing mixture. If the chloroform solution is boiled, or if the crystals are moistened with alcohol, the bromide is converted into *hydrobromide of pyridine bromide* ( $C_5H_5Br_2$ )<sub>2</sub>.HBr, which forms large red fragile plates melting at 125—126°, soluble in water, hydrochloric acid, alcohol and ether. It also dissolves in potash and in sodium carbonate, the original compound being precipitated from these solutions on addition of acids. By prolonged action of potash or by the action of hydrogen sulphide, the hydrobromide is converted into pure pyridine, b. p. 116°. It is decomposed by ammonia, with evolution of nitrogen, and when boiled with water, gives off ammonia.

The  $\beta$ -lutidine described by Oechsner also yields an unstable compound, which forms large red-brown crystals melting at 64°. These compounds are analogous to the hydrobromide of dibromonicotine dibromide,  $C_{10}H_{12}Br_2N_2$ .Br<sub>2</sub>.HBr, described by Huber. The nicotine tetrabromide of Cahours and Etard is most probably dibromonicotine dibromide. The analogy between these nicotine bromides and the pyridine bromides, indicates that nicotine contains a non-hydrogenised pyridine group.

C. H. B.

**Synthesis in the Quinoline Series.** By Z. H. SKRAUP (*Monatsh. Chem.*, 8, 381—385).—The preparation and properties of ortho- and para-toluquinoline have already been described (Abstr., 1880, 920). Metatoluquinoline has now been prepared by the same method from metatoluidine (42 grams), metanitrotoluene (27 grams), glycerol (100 grams), and sulphuric acid (90 grams). It is a pale yellow strongly refracting liquid boiling at 259.7° (corr.) under 747 mm. pressure; sp. gr. at 0° = 1.0839, at 20° 1.0722, at 50° = 1.0576. It does not solidify at -20°; its solution in dilute sulphuric acid shows a blue fluorescence. Its odour and other properties are very similar to those of orthotoluquinoline. The *platinochloride*,  $(C_{10}H_9N, HCl)_2, PtCl_4 + 2H_2O$ , forms brilliant orange-yellow prisms very sparingly soluble in cold, more so in boiling water, but the best solvent is boiling dilute hydrochloric acid. The *hydrochloride* crystallises with difficulty in thin white needles or large clear prisms, which are hygroscopic, soon become dull in the air, and carmine-red on exposure to light. *Sulphates*.—One crystallises from dilute alcohol in white prisms, insoluble in absolute alcohol, easily soluble in 60 per cent. alcohol; it is not a pure salt; another,  $(C_{10}H_9N)_2(H_2SO_4)_3$ , forms small thin deliquescent needles soluble in alcohol containing very little water. The picrate forms deep yellow microscopic prisms melting at 206—207° (uncorr.), almost insoluble in benzene and alcohol. The *methiodide*,



crystallises in long brittle light yellow needles, almost insoluble in

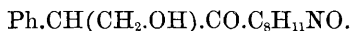
ether, sparingly in absolute, more easily in dilute alcohol, and most soluble in water; the alcoholic solution is yellow, the aqueous colourless. On adding alkali to the aqueous solution an oil separates out, and on boiling the usual quinoline odour is observed. In the following table the boiling points and specific gravities of the three known toluquinolines are compared:—

Toluquinoline	B. p. corr.	Bar.	Sp. gr.		
			0°.	20°.	50°.
From [1 : 2] toluidine..	247·3—248·3°	751·3 mm.	1·0852	1·0734	1·0586
From [1 : 3] toluidine..	259·7°	747·0 „	1·0839	1·0722	1·0576
From [1 : 4] toluidine..	257·4—258·6	745·0 „	1·0815	1·0681	1·0560
D. A. L.					

**Artificial Piperine.** By L. RÜGHEIMER (*Ber.*, **15**, 1390—1391).—*Piperine* can be prepared artificially by the action of piperic chloride on an excess of piperidine dissolved in anhydrous benzene. Piperidine hydrochloride is first deposited. The filtrate is washed with dilute hydrochloric acid, and with water. After removing the greater portion of the benzene by distillation, light petroleum is added to the residue until a precipitate is produced. The filtrate from this precipitate deposits crystals of piperine (m. p. 125—127°) on spontaneous evaporation.  
W. C. W.

**Action of Potassium Permanganate on Hydrapoatropine.** By L. PESCI (*Gazzetta*, 1882, 285—289; and 329—332).—The author has previously called attention to two derivatives of atropine, viz., apoatropine,  $C_{17}H_{21}NO_4$ , and hydrapoatropine,  $C_{17}H_{23}NO_2$ , the former being a product of the dehydration of atropine, obtained by pouring this base into fuming nitric acid heated to 50°, whilst the latter is formed by hydrogenation of apoatropine under the influence of sodium-amalgam.

Such being the relations between these bodies, it seemed probable that hydrapoatropine might be converted into an isomeride of atropine by oxidation with potassium permanganate. Ladenburg and Rügheimer have in fact shown that the group CH may be converted, by the action of permanganate in alkaline solution, into the tertiary alcoholic group COH, as in the transformation of hydratropic acid,  $Ph.CHMe.CO_2H$ , into atrolactic acid,  $Ph.C(OH)Me.CO_2H$  (*Ber.*, 1880, 373; *Abstr.*, 1880, 472); and this result seemed to indicate the possibility of converting hydrapoatropine,  $Ph.CHMe.CO.C_8H_{11}NO$ , into the compound  $Ph.C(OH)(CH_3).CO.C_8H_{11}NO$ , isomeric with atropine,



Experiment however showed that the action takes place in a totally different manner, for hydrapoatropine, even in a feebly alkaline solution, is quickly resolved into hydratropic acid and tropine; and when the bodies are brought together in neutral solution, the hydrapoatro-

pine loses  $\text{CH}_2$ , and is converted into a base  $\text{C}_{16}\text{H}_{21}\text{NO}_2$ , named by the author *homohydrapootropine*.

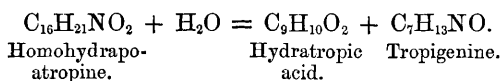
To prepare this base, 11.5 grams of potassium permanganate were added by small portions to a neutral solution of 10 grams of hydrapootropine in dilute sulphuric acid, the liquid being kept perfectly neutral by occasional addition of sulphuric acid. The reaction being completed, the liquid is to be filtered and evaporated to a small bulk in a stream of hydrogen. The base thus obtained is a dense, colourless, and inodorous liquid, slightly soluble in water, to which it imparts a strongly alkaline reaction and intensely bitter taste; easily soluble in alcohol and in chloroform. It absorbs carbonic anhydride from the air, and is converted into the compound  $(\text{C}_{16}\text{H}_{21}\text{NO}_2)_2\text{CO}_2$ , which may be obtained by passing carbonic anhydride into an alcoholic solution of the base, in mammelated groups of slender colourless transparent needles, becoming opaque in the exsiccator.

The *sulphate*,  $(\text{C}_{16}\text{H}_{21}\text{NO}_2)_2\text{H}_2\text{SO}_4 + x\text{H}_2\text{O}$ , crystallises in long colourless transparent needles, which effloresce in the exsiccator. It is easily soluble in water and in alcohol. The *hydrochloride* is very soluble in water and in alcohol, and crystallises in radiate groups of slender needles. The *aurochloride*,  $\text{C}_{16}\text{H}_{21}\text{NO}_2\text{HCl}\cdot\text{AuCl}_3$ , is very soluble in boiling alcohol, and crystallises on cooling in transparent yellow needles.—The *platinochloride*,  $(\text{C}_{16}\text{H}_{21}\text{NO}_2\text{HCl})_2\text{PtCl}_4$ , crystallises in fern-like groups of octohedrons, very slightly soluble in water.—The *chloropalladite*,  $(\text{C}_{16}\text{H}_{21}\text{NO}_2\text{HCl})_2\text{PdCl}_2$ , forms transparent roseate-yellow laminæ, very slightly soluble, even in hot water.

A neutral solution of the hydrochloride containing 1 per cent. homohydrapootropine, gives white precipitates with *tannic acid*, *Meyer's reagent*, and *cadmiopotassic iodide*; with *mercuric chloride*, a white precipitate, which crystallises in octohedrons soluble in boiling water; with *auric chloride* and with *picric acid*, yellow crystalline precipitates; with *potassiomericuric iodide* a red-brown precipitate which crystallises in long yellow prisms.

On dissolving a small quantity of homohydrapootropine in about ten times its bulk of fuming nitric acid, heating the liquid to the boiling point for a few seconds, then evaporating to dryness at a gentle heat, a viscid yellow residue is obtained, which gives a very deep persistent blood-red coloration with alcoholic potash. Atropine, apootropine, and hydrapootropine, similarly treated, gave a very fine violet coloration, changing to wine-red.

By saponification with barium hydrate, homohydrapootropine is resolved into hydratropic acid and tropigenine, the base which Merling lately obtained by the action of potassium permanganate on tropine (p. 739 of this volume):



H. W.

**Hüfner's Reaction with Bullock's Bile and some Properties of Glycocholic Acid.** By F. EMICH (*Monatsh. Chem.*, 3, 325—342)

—While preparing glycocholic acid by mixing bile with ether and hydrochloric acid (Hüfner's method), the author observed that some biles only deposited the acid after several days; he has therefore further investigated the subject. Of several examples of Graz galls, 50 per cent. gave the reaction in the first hour, 15 per cent. within a week, while the remainder did not show it at all. From an examination of 14 samples he infers that—1. The quantity of glycocholic acid which separates out is inversely as the time of crystallisation, *i.e.*, the quicker the crystallisation the larger the yield, &c. 2. Benzene is better than ether; with benzene and hydrochloric acid, the separation takes place more quickly, is more copious, and is even produced in those biles which give no precipitate with ether. 3. Cow bile gives crystals more frequently than ox bile, as Hüfner has already remarked. For a more complete examination of the biles he divides them into two classes; those which crystallise within half-an-hour he calls "crystallising biles," and those which do not do so within 24 hours are called "non-crystallising biles." In outward appearance and density they are alike. The following are the results of the quantitative examination of the two classes of bile:—

Constituent.	Crystallised bile.	Non-crystallised bile.	Remarks.
Water .....	92·44	91·42	Loss at 105° C.
Sodium glycocholate.	3·12	0·69	Calculated from the lead salt precipitate.
	3·00	—	Calculated from Hüfner's reaction precipitate.
Sodium taurocholate.	2·81	5·40	Calculated from sulphur found.
Mucine .....	0·24	0·22	Alcoholic extract, less ash of extract.
Inorganic salts .....	0·64	0·68	From ash after extraction of the bile acid salts.

The only important difference between the two classes of bile is therefore in the proportion of the glycocholic and taurocholic acids. The author therefore assigns as a reason for the non-crystallising biles not showing Hüfner's reaction, that they contain no more or very little more glycocholic acid than can be dissolved by the taurocholic acid set free on the addition of acid (see below, solubility of glycocholic acid in taurocholic acid).

*Solubility of Glycocholic Acid.*

In water—

Temperature of water .....	20°	60°	80°	100°
Glycocholic acid dissolved (per cent.)	0·033	0·102	0·235	0·85

In alcohol—

Strength of alcohol (per cent.) .....	1	2	10	20	30	50
Acid dissolved (per cent.)	0·035	0·049	0·10	0·275	1·674	27·53

4 m 2

In taurocholic acid—

Strength of solution employed (per cent.)	1	5	10
Glycocholic acid per cent. dissolved . . .	0.056	0.37	0.69

Ether, benzene, and chloroform at 20° C. dissolve respectively 0.093, 0.009, and 0.011 per cent. of glycocholic acid.

Strecker observes (*Handwörterbuch*, 2, 1192) that glycocholic acid melts above 100°, giving off water and forming glycocholononic acid. The author finds the melting point always constant at 132—134°, but has not remarked the loss of 3.9 per cent. (1 mol.) of water necessary for the above change. At 100—115° the loss in weight is insignificant; at 140—150°, after eight hours, it is 2.6 per cent.; at 160—170°, after two hours, it is 4.5 per cent. When a saturated solution of pure glycocholic acid is boiled with water for 24 hours, about 22 per cent. is converted into *paraglycocholic acid*. This acid (m. p. 183—184°) is nearly insoluble in water; the solution shows no reaction with litmus, and is tasteless, although the acid itself is intensely bitter. The dry substance adheres strongly to glass, and appears to be a very bad conductor of electricity. Titration with soda (the glycocholates are neutral) proves that glycocholic acid is monobasic.

D. A. L.

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## Physiological Chemistry.

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**Gastric Juice.** By P. CHAPOTEAUT (*Compt. rend.*, **95**, 140—141). —The author has previously found (*ibid.*, **94**, 1722) that an aqueous solution of gastric juice previously dried and washed with ether, yields a pulverulent white precipitate when mixed with its own volume of alcohol. Since alcohol modifies the precipitate, it is better to use sulphuric acid or some other acid which does not dissolve the precipitate if added in excess; excess of hydrochloric acid readily dissolves it. This white precipitate constitutes the active part of the gastric juice. In presence of a small quantity of lactic acid it converts beef fibrin into syntonin in five or six minutes, and into peptone if heated to 60°. A litre of water dissolves 2 grams at the ordinary temperature, and the aqueous solution is not coagulated at 100°. At this temperature, however, the substance loses its fermentative power. The substance is soluble in alkalis, and is reprecipitated by acids, but gradually loses its active properties. It is also precipitated by lime, baryta, and basic lead acetate. It exerts no action on polarised light, and contains C 51, H 7.2, N 15.4 per cent. Its composition is therefore similar to that of the albuminoids. It may be regarded as true *pepsin*, and exists in the gastric juice in the form of potassium salt, together with another albuminoid which does not dissolve blood-fibrin, and a fatty acid which cannot displace the pepsin from its combination with potassium.

C. H. B.

**"Acidity" of Blood-serum and other Animal Fluids.** By R. MALY (*Monatsh. Chem.*, 3, 309—324).—Some results on this subject have already been published (Abstr., 1878, 594). The author remarks that blood-serum contains sodium-hydrogen carbonate, therefore when the serum is titrated with an acid, every atom of "acid" hydrogen of the acid displaces 1 mol. of carbonic anhydride, so that for every equivalent of acid added, two equivalents are driven off; moreover, the normal alkaline carbonates (and phosphates) have an abnormal (alkaline) reaction on litmus. For these reasons the ordinary titration of serum is not trustworthy. He has therefore adopted the following method of analysis: the serum is treated with a measured quantity of standardised dilute soda to convert the acid carbonates and phosphates into normal salts. The carbonic and phosphoric acids are then precipitated with barium chloride, and are filtered off. The filtrate is titrated with acid until neutral. The difference between the amount of alkali found and the quantity added will be the quantity neutralised by the acids in the serum. In a series of experiments he has obtained the following results:—

Indicator.	50 c.c. require milligrams of sodium hydrate				
	Human serum.	Bullock's serum.			
		1.	2.	3.	4.
Litmus .....	54·4	54·4	43·5	34·8	38·0
Phenolphthalein .....	74·1	74·7	59·8	58·7	59·8

which show that serum has acid properties. It will be observed that the indicator used makes a great difference, phenolphthalein always giving higher results than litmus; this is probably due to the different effect exerted by albuminoids. Hinteregger has shown that acids and acid salts diffuse more readily than neutral salts, therefore blood-serum containing acids ought to yield an acid diffusate. This the author has found to be the case. 350 c.c. serum dialysed in distilled water yielded a diffusate containing sufficient acid to neutralise 212 mgrms. of soda. Similar experiments with bile both by titration and dialysis tend to prove that this fluid is also "acid."

These experiments confirm the conclusions which Zuntz drew from his experiments on serum with the exhaust pump. D. A. L.

**Peptonisation of Albuminoids in Koumiss.** By A. DOCHMANN (*Bied. Centr.*, 1882, 503).—In 1000 parts of fresh and fermented mare's milk were found—

	Fresh.	12 hours' fermentation.	40 hours.	70 hours.
Casein .....	24·8	14·66	12·88	9·64
Albumin .....		3·02	2·03	1·20
Parapeptone — syntonin .	—	4·88	8·40	6·88
Peptone.....	0·28	1·04	2·48	4·84

E. W. P.

**Poisonous Action of Hydroxylamine.** By C. RAIMONDI and G. BERTONI (*Gazzetta*, 12, 199—203).—The toxic action of hydroxylamine is acute or slow, according to the dose and the manner of administering it. Direct injection into the vein in doses of 30—40 mgrms. causes death in a few seconds in the case of a chicken, 150—200 mgrms. being required to produce the same effect with a moderate sized dog. By hypodermic injection, the action is slower, death taking place after a lapse of some time with collapse and slow asphyxia, preceded by a stage of excitement. Dogs recover from comparatively large doses administered by hypodermic injection; an animal of 7 to 8 kilos., to which 200 to 300 mgrms. had been administered in this way, suffered from partial asphyxia, but in two or three days it was as usual.

In poisoning by hydroxylamine, two stages are observed, the first, one of excitement, and this is succeeded by a state of collapse with symptoms of asphyxia; the blood becomes yellowish, and in some cases there is congestion of the inferior lobes of the lungs. The blood, when examined microscopically, shows that the colour of the red globules is altered, but not their form, except in cases of slow asphyxia.

If hydroxylamine hydrochloride is added to a solution of normal blood, it instantly changes the colour from rose-red to a yellowish tint, and spectroscopic examination shows that the two bands characteristic of oxyhæmoglobin have disappeared. If ammonium sulphide is added to this solution, no change is produced; but if hydroxylamine hydrochloride is added to a blood solution previously reduced by ammonium sulphide, it effervesces, and changes colour from red to green; at the same time, the bands characteristic of the reduced blood disappear and another narrower and sharper band appears in the red. The yellowish-brown blood from an animal poisoned with hydroxylamine, or blood to which the reagent has been added not in excess, still shows the bands characteristic of oxyhæmoglobin, but only faintly as compared with normal blood. From these experiments, it will be seen that although the hydroxylamine becomes oxidised to nitrous acid (comp. p. 1231), it does not behave with blood like the ordinary reducing agents; neither is its action similar to that of carbonic oxide, nitrogen dioxide, or hydrocyanic acid, for these form compounds with hæmoglobin, which may be obtained in the crystalline state, and are characterised by particular absorption spectra. It acts more like amyl nitrite, and deprives the hæmoglobin of the property of crystallising. The author concludes with some observations on



diagnosis of poisoning by hydroxylamine, and the remedies to be employed. C. E. G.

**Theory of the Poisonous Action of Arsenic.** By H. SCHÜLZ (*Ber.*, 15, 1388—1390).—The following table shows the relative energy with which arsenious oxide is oxidised to arsenic, and arsenic oxide reduced to arsenious, by different portions of the animal system:—

	+ 0.	— 0.	+ 0 : — 0.
Blood .....	0·0839	11·9228	0·007 : 1
Mucous coating of the stomach (swine) .....	0·2076	4·9615	0·040 : 1
Pancreas (swine) .....	0·2960	3·4863	0·080 : 1
Brain (calf) .....	0·3188	3·2116	0·090 : 1
Liver (calf) .....	0·6860	1·4576	0·470 : 1

It is only living protoplasm that can oxidise arsenious oxide. Arsenic oxide is more powerfully reduced by dead than by living tissues, because the dead protoplasm has lost its power of re-oxidising the arsenious oxide. W. C. W.

**Constituents of the Ashes of Cockchafers.** By F. FARSKY (*Bied. Cent.*, 1882, 492).

K <sub>2</sub> O.	Na <sub>2</sub> O.	CaO.	MgO.	Fe <sub>2</sub> O <sub>3</sub> .
10·74	3·39	13·41	11·33	6·48
P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	Cl.	SiO <sub>2</sub> sol.	SiO <sub>2</sub> insol.
42·09	11·12	0·38	1·67	0·13
				E. W. P.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Alteration of Nitric Ferment by Cultivation.** By R. WARINGTON (*Bied. Centr.*, 1882, 436).—Nitrification occurs readily when the solution is sufficiently dilute (80 mgrms. ammonium chloride per litre), and when the column of liquid is not too high (4—5 inches). If, however these conditions are altered, then nitrites are produced, and the amount increases as the temperature rises. If the solutions which are intended for starting nitrification in new ammonia solutions be kept for many months, nitrates are not produced, but only nitrites, which are not converted into nitrates; nitrified solutions when kept show a formation of a fibrous mould on their surface, and this mould instantly transforms nitrites into nitrates; this mould appears therefore to be a part only of the fermentation process, which evidently occurs by several steps.

E. W. P.

**Effect of Pruning the Tops and Roots of Fruit Trees on their Development.** By V. T. MAGERSTEIN and F. BILEK (*Bied. Centr.*, 1882, 477—480).—Trees with uncut tops produce a larger quantity of reserve matter, and clipping the roots has a like effect. Healthy fruit trees should have their roots cut but not their tops, whereas in the case of stone-fruit trees the tops may be pruned with advantage. E. W. P.

**Steeping of Barley.** By K. MICHEL and J. HANDWERCK (*Bied. Centr.*, 1882, 486).—Distilled water removes as much inorganic matter as spring water (containing 0·305 gram inorganic, and 0·12 gram organic matter per litre); distilled water containing 1 per cent. sodium chloride removed most organic matter, and distilled water least. The researches also show that sodium chloride acts as a solvent on the albuminoid matter, and that the presence of calcium salts prevents the entrance of the sodium chloride into the grain. Soft water does not remove more matter from the grain than hard water. Experiments also show that the presence of sodium chloride retards germination. E. W. P.

**On Dari.** By M. C. LEEUW (*Bied. Centr.*, 1882, 484).—The following analyses represent the composition of Egyptian and Syrian "Dari" (*Sorghum tartaricum*), also of malted dari, and the hulls of this grain:—

	Egyptian.	Syrian.	Malted.	Hulls.
Water .....	10·05	9·97	8·04	5·65
Nitrogenous matter.....	7·05	9·88	10·31	3·91
Fat.....	6·11	3·52	4·42	0·95
Nitrogen-free extract .....	74·20	72·22	73·32	25·58
Fibre.....	0·97	1·63	1·77	25·80
Ash .....	1·62	2·78	2·14	7·98
Starch .....	—	—	—	30·13
	100·00	100·00	100·00	100·00

One specimen from Zanzibar contained 66·69 per cent. starch.

E. W. P.

**Composition of Globularia.** By E. HECKEL and others (*Compt. rend.*, 95, 90—93).—The leaves dried at 100° have the following composition:—

Soluble in carbon bisulphide—	
Fat and wax.....	2·850
Soluble in ether—	
Traces of tannin and colouring matters, globularin, and cinnamic acid.....	2·438
Soluble in chloroform—	
Traces of tannin and colouring matters, globularin, and cinnamic acid.....	11·365
Soluble in alcohol—	
Mannitol .....	1·815
Glucose.....	2·585
Globularin .....	4·550
Tannin .....	2·000
Colouring matter and resin .....	17·000
Cinnamic acid .....	1·750
Loss .....	0·850
Soluble in water—	
Gum and amylaceous bodies .....	0·850
Insoluble resin.....	1·250
Ash .....	2·105
Water .....	26·200
Woody fibre.....	13·092
	<hr/>
	100·000

The tannin is ordinary tannin, the globularitannic acid of Walz being a mixture of tannin and colouring-matter. When boiled with dilute acids, globularin yields only one decomposition product, *globularetin*, and not two as stated by Walz. Globularetin when freshly prepared is oily or resinous, but after some time changes into a transparent amorphous mass. When dissolved in hot solutions of caustic alkalis, it combines with the elements of water, forming cinnamic acid. The leaves also contain another volatile aromatic substance, apparently benzyl cinnamate, but a quantity sufficient for examination was not obtained. The general composition of *globularia* is similar to that of the trees which yield the balsams of Peru, Tolu, and Storax.

C. H. B.

**Four-course Rotation.** By A. VÖLCKER (*Bied. Centr.*, 1882, 437—442).—These experiments made in 1880 form the continuation of those made in 1876—1879:—

*Rotation I. Barley.*—The previous crop of turnips had been manured with (plot 1) farmyard manure produced by the consumption of 784 kilos. chaff, 2268 kilos. turnips, 567 kilos. wheat-straw chaff, and 454 kilos. decorticated cotton cake. On plot 2 the manure was produced by cattle fed as above, with the exception of the cake which was replaced by 454 kilos. maize. On plot 3 with manure from the same as plot 1, but without the cake superphosphate, Chili saltpetre, potassium and magnesium sulphate, were added in quantities equivalent to two-thirds of the nutriment in the cotton-

cake. Plot 4 received the same as 2, without maize, which was replaced by artificials. The results were satisfactory; cotton-cake was better than maize; top dressing with saltpetre raised the yield of straw, but not of grain. On the maize plot, the percentage of small grain seems to be higher than on the others.

*Rotation 2. Wheat.*—The clover of the previous year was fed off by sheep, which had also received on plot 1 cotton-cake, and on 2 maize. To the other plots was added a mixture of "minerals," as for the barley during the autumn of 1879, whilst Chili saltpetre was added in the spring of 1880. The yield of wheat was low, due to bad seasons, but 1 and 3 gave lower results than 2 and 4 (artificials). The Chili saltpetre increased grain and straw.

*Rotation 3. Turnips* (previous crop, wheat).—The manure applied was the same as in Rotation 1, 1879; the yield was good, especially on the nitred plots.

*Rotation 4. Clover Rye-grass* (previous crop, barley).—Sheep were grazed on these plots in the previous season, receiving also on plot 1, cotton-cake; on plot 2 maize. Maize-meal produced a larger increase in live-weight.

5th experiment, year 1881 :—

*Rotation 1. Clover* (previous crop, barley).—In this year we find that sheep receiving cotton-cake in addition did better than those getting maize, which is, however, a good feeding stuff.

*Rotation 2. Roots* (previous crop, wheat).—Manures as before. The highest yield was on plot 3, to which was given the mineral matters of cotton-cake, and two-thirds of the nitrogen contained in the cake.

*Rotation 3. Barley.*—Manuring as before. The yield of grain was nearly equal on all the plots, but the nitrogen as Chili saltpetre considerably increased the yield of straw on 3.

*Rotation 4. Wheat* (previous crop, seeds).—Here, again, the yield of grain was fairly equal on all the plots, although on plot 3 (nitre) it was higher, as was also the yield of straw.

E. W. P.

**Continuous Growth of Wheat and Barley at Woburn in 1881.** By A. VÖLCKER (*Bied. Centr.*, 1888, 442—444).—Wheat and barley received the same manures, which included farmyard manure, produced by six bullocks, and mixtures of artificials so arranged as to show the difference of the action of Chili nitre and ammonia salts. The crops of wheat surpassed those obtained in former years; the very high yield from the unmanured plots is remarkable, and the more so, as this is the sixth year since manure was applied; but the season was very favourable. The highest yield is from the plot which received minerals and much nitre, but even with one-half the quantity of Chili nitre the results were high. Chili nitre produced better results than ammonia salts alone, or in combination; this is in opposition to the results of the previous year. "Minerals" alone were of no great value.

E. W. P.

**Examination of a Mixture of Weed-seeds used as Fodder.** By F. NOBBE (*Bied. Centr.*, 1882, 472).—A mixture of weed-seeds

which had been employed as food for cattle, consisted of 19·7 per cent. of sand, dust, mouse-dung, &c., the rest being seeds of chenopodium, &c. Such a mixture is useless as food, as it is quite indigestible, the seeds passing through the animals unaltered. If it be absolutely necessary to employ such material, it should be passed through a sieve and ground.

E. W. P.

**Changes Effected by Frost on the Composition of Potatoes.**  
By BIRNER (*Bied. Centr.*, 1882, 493).

	Fresh.	Fermented.	
		Steamed.	Unsteamed.
Water .....	70·89	68·43	54·15
Albuminoïds .....	2·00	2·15	1·61
Fat .....	0·11	0·07	0·06
Extractive matter .....	25·25	25·22	34·72
Fibre .....	0·61	0·75	0·774
Ash .....	0·88	1·19	1·17
Sand.....	0·26	2·19	7·52

1 kilo. of steamed potatoes contained 8·3 grams of lactic acid, while in the unsteamed there were only 3·2 grams.

E. W. P.

**Daily Rainfall.** By F. AUGUSTIN (*Bied. Centr.*, 1882, 433).—Comparisons of the hourly rainfall at Prague, Modena, Berne, Vienna, and Zechen, show the following results:—There are three maxima and minima of frequency and amount of rainfall. The first minimum of frequency occurs at midnight to 1 A.M., the minimum of quantity occurs at 2—3 A.M. The first maximum of frequency occurs soon after the minimum of temperature has been reached, viz., 6—7 A.M., whilst the maximum of quantity occurs at 7—8 A.M. The second minimum of frequency and quantity appears on the average to take place at midday. The second maxima of fall and frequency is simultaneous, being at 4—5 P.M.; with the exception of Berne, this is true for quantity all the year round at the other stations, but only at times during summer and winter for frequency. The third minimum takes place at about 7 P.M., and this minimum is the principal one during autumn for frequency. The third maximum of frequency occurs at 8—9 P.M., that of quantity 9—10 P.M. During spring, the evening maximum of frequency is everywhere the chief one.

E. W. P.

**Effects of Artificial Manures on the Physical Condition of Soils.** By E. WOLLNY (*Bied. Centr.*, 1882, 435).—In a fertile soil, the particles are not closely laid together, but are loosely united in a crumbly condition, so that passages for air and water exist. Ammonia, alkalis, phosphates, and carbonates of the alkalis prevent the formation of this condition, as the clay held in suspension by water is by these salts caused to settle down in a compact layer; on the other hand,

small quantities of mineral acids and their salts cause the precipitation of clay to be flocculent. Thus the passages in the soil are not closed. Large quantities of chlorides and nitrates, and sulphates, however, are prejudicial to the fertility of fine-grained soils. E. W. P.

**Experiments with so-called "Dissolved Wool."** By A. PETERMANN (*Bied. Centr.*, 1882, 454—458).—On heating waste wool from manufactories by superheated steam, a considerable amount of the nitrogen present becomes soluble, the greater part not in the form of ammonia. The effect of this substance as a manure was found to be very advantageous, comparing favourably with sodium nitrate. In open sandy soils, owing to the combination in which the nitrogen exists, no large amount is lost by drainage. E. W. P.

**Agricultural Value of various Forms of Phosphoric Acid.** By E. WILDT (*Bied. Centr.*, 1882, 460—462).—The experiments were conducted at 22 stations in Posen, but only a few of the most satisfactory results are quoted. The manures were ammonium sulphate alone; sulphate and a small quantity of soluble phosphate; the same with reduced phosphate in addition; ammonium sulphate and a treble quantity of soluble phosphate; and lastly, sulphate with precipitated phosphate. The crops were barley, oats, and potatoes. Generally, there was no great difference between reduced and precipitated phosphate, but the soluble form produced much larger crops. The results are in opposition to those of Märcker, who found that, practically, soluble, reduced, and precipitated phosphates were alike. The author accounts for the difference by the presence of the nitre used, which may have rendered the insoluble forms more soluble. E. W. P.

**Manuring with Phosphates in the Département du Nord.** By LADUREAU (*Bied. Centr.*, 1882, 452).—It is generally supposed that it is useless to apply phosphates to the soil of this district, and it is customary only to add nitrogenous manures. Analysis of some of the soils shows the absence of phosphoric acid, and experiments proved that the application of superphosphate was decidedly advantageous. The undissolved phosphates were useless, owing to the neutral or alkaline character of the soil; the crop was sugar-beet. Ammonium sulphate and superphosphate produced a yield two-thirds higher than that from unmanured plots; although the sugar per decilitre of juice was much lower, yet the total weight of sugar per hectare was much greater. E. W. P.

**Action of Soluble and Insoluble Phosphates on Swedes.** By A. VÖLCKER (*Bied. Centr.*, 1882, 458—460).—The experiments conducted at Woburn on swedes show that dissolved "coprolites" were better than the undissolved, moreover, they were better than any other phosphatic manure, except a mixture of superphosphate and guano, the price of which is, however, double that of the others. Redonda phosphate produced slightly higher yield than coprolites, and it was better than bone-meal. The results with precipitated phosphate were most unsatisfactory. E. W. P.

**Manuring with Saltpetre, Superphosphate, and Precipitated Phosphate.** By H. LÖBBEKE (*Bied. Centr.*, 1882, 491).—The best results were obtained with saltpetre and precipitated phosphate; the addition of superphosphate to the saltpetre produced no increase. No statement concerning the soil is given. E. W. P.

**New Source of Phosphoric Acid.** By MÄRCKER (*Bied. Centr.*, 1882, 490).—In the slag formed by the dephosphorising of iron there is found 12–18 per cent. of phosphoric acid; the slag is strongly alkaline, and slowly falls to powder in the air. From this, ammonium citrate removes 4·4 per cent., and dilute acetic acid 1·44 per cent. This substance is adapted for soils containing but little lime, and may be obtained in a more concentrated form, so as to reduce transport expenses. In one factory alone 5·6 million kilos. of the phosphoric acid are lost annually by not working up the slag. E. W. P.

**Analysis of the Stassfurth Manure Salts.** By F. FARSKY (*Bied. Centr.*, 1882, 490).

	Concen- trated potash manure.	Thrice con- centrated potash manure.	Five times con- centrated.	Purified potassium sulphate.	Purified potassium magnesium sulphate.
CaSO <sub>4</sub> .....	0·69	1·38	0·25	0·62	0·58
MgSO <sub>4</sub> .....	12·35	8·02	0·20	0·38	36·28
K <sub>2</sub> SO <sub>4</sub> .....	23·15	—	—	97·20	53·17
MgCl <sub>2</sub> .....	1·15	2·40	0·25	—	—
KCl .....	22·95	52·38	82·57	0·35	0·23
NaCl .....	32·34	26·30	14·23	—	3·52

E. W. P.

**Composition of Materials adapted for Composts.** By PETER-MANN (*Bied. Centr.*, 1882, 462).—Approximate analyses of various waste materials which may be used advantageously for composts.

E. W. P.



## Analytical Chemistry.

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**A New Apparatus for Gas Analysis.** By W. N. SOKOLOFF (*Ber.*, 15, 1167—1172).

**Improved Slit for Spectroscope.** By H. KRÜSS (*Zeits. Anal. Chem.*, 21, 182).—An ingenious slit with symmetrical movements of the edges is figured and described, intended for use in quantitative spectrum analysis. The description is not readily intelligible without the accompanying drawings. O. H.

**Preparation of Standard Acid.** By O. KNUBLAUCH (*Zeits. Anal. Chem.*, **21**, 165).—Neutral ammonium sulphate is recommended as the basis for ascertaining the strength of the acid. The salt crystallises very readily, without water of crystallisation, is not hygroscopic, and can be dried at 100° without decomposition. The author liberates the ammonia from a weighed quantity of the salt, and distils the same into the acid to be tested. He uses with advantage the form of apparatus described by him (see below). O. H.

**Expansion of various Standard Solutions by Heat.** By A. SCHULZE (*Zeits. Anal. Chem.*, **21**, 167).—P. Casamajor has shown that in exact volumetric analyses corrections for the expansion of the solutions by heat must not be omitted, and he recommends the use of the factors ascertained for the expansion of water at various temperatures. In the present paper the author has carefully ascertained by means of Kopp's dilatometer, as modified by Ostwald, the expansion of various normal solutions, and finds that many of them deviate in this respect very widely from pure water. He gives tables of corrections for a large number of solutions used in volumetric analysis. They are calculated for a normal temperature of 17.5° C, and the cubical coefficient of expansion of glass is taken as 0.000029, the number, 0.000026, usually given, being too small for the kinds of glass ordinarily used. O. H.

**Estimation of Chlorine in Presence of Iodine and Bromine.** By G. VORTMAN (*Ber.*, **15**, 1106).—A mixture of potassium chloride with lead dioxide is not decomposed by evaporation with a 2—3 per cent. solution of acetic acid, even when the evaporation is repeated five or six times, whilst potassium iodide, when so treated, is very readily decomposed, and potassium bromide, although with greater difficulty, is still completely decomposed if the evaporation is repeated once or twice. By use of 5 per cent. acetic acid, potassium chloride is decomposed with difficulty. Similarly, manganese dioxide with 2—3 per cent. acetic acid, readily decomposes potassium iodide, but has not the slightest action on potassium bromide. With acid of 10 per cent. only traces of bromine are liberated. (*Comp. Abstr.*, 1880, 509; and this vol., 1132.) A. J. G.

**Estimation of Ammonia by Distillation.** By O. KNUBLAUCH (*Zeits. Anal. Chem.*, **21**, 161).—The author has constructed a distillation apparatus, allowing of very rapid operation. It consists in the main of a distillation flask, and a very wide cylindrical absorption vessel, rendering the sucking back of the acid into the flask impossible. A number of ammonia determinations are quoted, the results of which are very satisfactory. O. H.

**Absorbents for Nitric Oxide.** By C. BÖHMER (*Zeits. Anal. Chem.*, **21**, 212).—A solution of ferrous sulphate is generally employed for the absorption of nitric oxide for analytical purposes, but is inconvenient on account of the bulk of fluid necessary. Saturated solutions of potassium permanganate or of chromic acid are found to act more rapidly and vigorously, the former salt being especially con-

venient, as an alkaline solution absorbs both carbonic anhydride and nitric oxide at the same time. (G. Lunge has already recommended potassium permanganate for the same purpose.) O. H.

**Detection of Nitrous Acid in the Blood.** By G. BERTONI and C. RAIMONDI (*Gazzetta*, 12, 195—198).—The opinion set forth by one of the authors that the poisonous action of hydroxylamine on the animal economy is due to its becoming oxidised to nitrous acid at the expense of the oxygen in the blood, rendered it necessary to find some good process for detecting nitrous acid in blood. The methods proposed by Schonbein, Hoppe-Seyler, and Bence Jones for detecting nitrous acid in animal fluids being eminently unsatisfactory, the authors submitted the blood to dialysis, and then examined the dialysed liquid with starch and potassium iodide in the usual manner; this was perfectly successful. The dialysed solution may be examined directly, but it is better to evaporate to dryness at  $100^{\circ}$ , and take up the nitrite with hot alcohol: in this way traces of albuminoid substances are removed, which have passed through the dialyser as albuminates. The residue dried at  $100^{\circ}$ , moreover, gives off nitrous fumes on adding an acid, so that there can be no doubt as to the oxidation of hydroxylamine to nitrous acid in the blood. C. E. G.

**Detection of Sulphurous Acid in Wine.** By V. WARTHA (*Ber.*, 15, 1398—1401).—A reply to L. Liebermann's criticisms on the author's method for the detection of sulphurous acid in wine (*Ber.*, 15, 437). W. C. W.

**Estimation of Phosphoric Acid.** By C. MOHR (*Zeits. Anal. Chem.*, 21, 216).—The author recommends Joulie's plan for the estimation of phosphoric acid, which consists in titrating the phosphoric acid by means of uranium in the ammonium magnesium precipitate, instead of weighing the same. The examples given are not satisfactory. O. H.

**Estimation of Potassium as Platinochloride.** By R. FRESENIUS (*Zeits. Anal. Chem.*, 21, 234).—The atomic weight of potassium has been lately revised by Seubert (*Annalen*, 207, 1), and found to be 39.032 ( $H = 1$ ,  $O = 15.96$ ,  $Cl = 35.365$ ), corresponding to 30.697 per cent. of potassium chloride in the platinochloride precipitate. According to Berzelius, 100 parts of potassium platinochloride contain 30.58 parts of potassium chloride; Andrews gives 30.51 per cent., and Fresenius (*Quantitative Analysis*, 6th ed.), 30.56.

Without entering into a discussion as to the accuracy or the relative merit of the various statements, the author has undertaken a series of very carefully conducted experiments to ascertain which proportion yielded the best results in actual analytical practice, and he finds that the weight of the potassium platinochloride (dried at  $130^{\circ} C.$ ) multiplied by 0.3056, exactly corresponds with the amount of potassium chloride employed, whilst Seubert's figures give results which are about half a per cent. too high. O. H.

**Methods for the Detection of Cadmium in Presence of Copper.** By A. ORLOWSKI (*Zeits. Anal. Chem.*, **21**, 214).—*First Method.*—The blue solution obtained in qualitative analysis after removal of the bismuth is acidified with hydrochloric acid, stannous chloride is added until it becomes colourless, and the fluid is boiled with milk of sulphur. All copper is precipitated as sulphide, and the filtrate, after removal of the tin by precipitation with ammonia, is tested for cadmium with hydrogen sulphide.

*Second Method.*—The ammoniacal solution containing copper and cadmium is acidified with hydrochloric acid and heated with thiosulphate until the precipitate has become dark brown, but not black, and the solution is clear and colourless. The filtrate contains the cadmium.

G. Vortmann has already described the latter method (*Zeits. Anal. Chem.*, **20**, 416). O. H.

**Detection of Cuprous in Presence of Cupric and other Metallic Oxides.** By A. ORLOWSKI (*Zeits. Anal. Chem.*, **21**, 215).—The solution to be tested is acidified with hydrochloric acid and boiled with milk of sulphur. Only cuprous, but not cupric salts, are affected, the former being precipitated as sulphide. In case of fluids which would be altered by boiling, a piece of sulphur is simply suspended in the solution for 10—12 hours. It becomes black in the presence of cuprous salts. O. H.

**Determination of Impurities in Metallic Copper.** By R. FRESSENIUS (*Zeits. Anal. Chem.*, **21**, 229—234).—100 grams of the sample are treated with pure nitric acid of 1.2 sp. gr. The filtrate is collected in a tared flask graduated to hold 2000 c.c. The residue insoluble in nitric acid is fused with sodium sulphide and sodium carbonate, and the melted mass lixiviated with water. The black residue which remains is oxidised with nitric acid, and from the solution the silver is precipitated with hydrochloric acid, the lead with sulphuric acid, and from the filtrate bismuth by sulphuretted hydrogen. The sulphide solution containing antimony, tin, and arsenic, is precipitated with hydrochloric acid, and the precipitate, consisting of sulphides and free sulphur, is treated with a hydrochloric bromine solution. From this solution, the metals are again precipitated as sulphides, dissolved in ammonium sulphide, the solution is evaporated in a porcelain crucible, and the residue fused with sodium hydroxide and nitrate. The antimony is weighed as sodium antimonate, tin and arsenic being separated according to H. Rose's method.

To 1 litre of the copper solution, corresponding with 50 grams of the sample, four drops of hydrochloric acid are added. Any chloride of silver is allowed to settle, and the silver determined as metal, the amount being added to that found in the nitric acid residue. To the filtrate from the silver chloride, 85 grams pure sulphuric acid previously diluted with water are added, and the solution is evaporated to remove all nitric acid. The residue is treated with water until all cupric sulphate has gone into solution, and filtered from the insoluble

*lead* sulphate, which is weighed as such. It should be entirely soluble in ammonium acetate. The filtrate from the lead is made up to 2 litres, and divided into 4 equal portions, each portion being then diluted with about an equal bulk of water, acidified with 50 c.c. hydrochloric acid of 1.12 sp. gr., and precipitated with sulphuretted hydrogen at 70° C. The contents of the four flasks are then washed into a weighed stoppered flask holding about 6 litres, and the whole is again weighed. After allowing the precipitate to settle, the fluid is drawn off as completely as possible, the remaining quantity being weighed to ascertain the weight of the drawn-off solution. The latter is evaporated in a porcelain basin, and the residue heated until most of the free sulphuric acid has been driven away. It is then heated with a little nitric acid, and the *iron* is precipitated with ammonia, the oxide being redissolved and again precipitated. In the filtrate from the iron precipitate, *nickel*, *cobalt*, and *zinc* are determined as usual.

Soda is added to the precipitated sulphide in the weighed flask until the solution is alkaline, then sodium disulphide, and the whole is gently heated. It is then diluted with much water, the precipitate allowed to settle, and from the weighed total the clear fluid is drawn off and also weighed: the sulphides of *tin*, *arsenic*, and *antimony* are again precipitated from it by hydrochloric acid and separated as described, the amounts found being added to the portions already estimated.

The principal sulphide precipitate (containing the copper) is washed with dilute sodium sulphide solution, dissolved in nitro-hydrochloric acid, and the solution evaporated with an excess of hydrochloric acid; the saline residue is then treated with water, the *bismuth* remaining undissolved mixed with some copper: this is dissolved in hydrochloric acid, alkali is added until the reaction is alkaline, and cyanide of potassium in excess. The bismuth can then be precipitated from the solution as sulphide, free from copper.

400 c.c. of the original nitric acid solution (corresponding to 20 g. of copper) are nearly neutralised with ammonia, and a few drops of barium nitrate are added. If the copper contain any *sulphur* (present according to Hampe in the form of sulphurous acid) a precipitate of barium sulphate is obtained, which is weighed. But as barium sulphate is slightly soluble in copper nitrate solution, it is necessary to treat the copper in a current of chlorine in order to detect very small traces of sulphur.

Another quantity of 400 c.c. of the original solution is repeatedly evaporated with hydrochloric acid, the residue is dissolved in about 1200 c.c. water, and the solution is precipitated with sulphuretted hydrogen: the *phosphoric acid* in the filtrate is precipitated with molybdc solution as usual.

O. H.

**Alkalimetric Titration of Potassium Dichromate, and Use of the Salt in Alkalimetry.** By M. RICHTER (*Zeits. Anal. Chem.*, 21, 205).—If phenolphthaleïn be used as an indicator, potassium dichromate may, as test experiments show, be accurately titrated with standard alkali. *Vice versâ*, dichromate may be conveniently used to ascertain the strength of alkaline fluids.

O. H.

**Estimation of Chromium.** By F. P. TREADWELL (*Ber.*, 15, 1392—1393).—Accurate results were obtained in estimating chromium in the form of sesquioxide by precipitation with ammonia, when the operation was carried on in glass vessels. Wilm's (*Ber.*, 12, 2223) statement that under these conditions the results are always 3—6 per cent. too high is therefore inaccurate. W. C. W.

**Separation of Nickel and Cobalt.** By A. JORISSEN (*Zeits. Anal. Chem.*, 21, 208).—The action of reducing agents on nickel hydroxide is, as is well known, much more vigorous than on cobalt oxide. Thus potassium cyanide readily dissolves the former, but is without action on the latter. From large quantities of cobalt the nickel may conveniently be separated as follows:—The hydroxides are precipitated from the solution by potassium hydroxide and bromine; to the precipitate a few cubic centimeters of potassium cyanide solution are added, and the mixture is well shaken at ordinary temperature. The filtrate is evaporated with nitro-hydrochloric acid, and in presence of nickel gives all reactions of the metal. When the nickel is in great excess, some of the cobalt also goes into solution. O. H.

**Precipitation of Titanic Acid.** By P. T. AUSTEN and F. A. WILBER (*Amer. Chem. J.*, 4, 211—214).—The authors recommend the following process:—The ore is fused with alkaline carbonates and nitrates, and after digestion with water in the usual way, the solution is acidified with hydrochloric acid and evaporated to dryness to render silica insoluble. The residue is then moistened with hydrochloric acid and treated with a little warm water till the soluble parts are taken up, after which it is left to cool, and then diluted, without filtering, to 400—500 c.c.; sulphurous acid is next added, and then 50 to 60 c.c. of acetic acid. On boiling in the usual manner, the titanic acid will be precipitated in a flocculent and filtrable state. The whole is then to be filtered and washed with hot water containing a little acetic acid. If the ore does not contain phosphoric acid, the precipitate will be quite free from iron, and after expulsion of the silica by treatment with ammonium fluoride and sulphuric acid, is generally pure enough to be taken as titanic acid, although in certain cases, where the amount of titanic acid is small and that of iron large, a second fusion may be necessary. If the ore contains phosphates, the titanic acid precipitate will always contain iron and phosphoric acid. In this case, the residue left after expelling the silica with ammonium fluoride, may be fused with sodium carbonate, and the melt exhausted with water, which dissolves the sodium phosphate and leaves the sodium titanate and ferric oxide. The residue is then fused with a little sodium bisulphate, and the titanic acid precipitated after reduction by boiling. The filtrate containing the iron which was precipitated with the silica is now added to the filtrate from the original precipitation of the titanic acid, and to the acidified filtrate from the fusion of the titanic acid with sodium carbonate; and the united solutions, after having been freed from potassium by precipitation with hydrogen sulphide, are analysed for alumina, iron, manganese, lime, and magnesia. H. W.

**Preparation of Copper for Elementary Analysis.** By F. WEYL (*Ber.*, 15, 1139—1140).—Metallic copper prepared by the reduction of copper oxide in hydrogen contains, as is well known, not inconsiderable quantities of hydrogen; by reducing copper oxide in a stream of formic acid vapour, metallic copper is obtained quite free from hydrogen. A. J. G.

**Contributions to Wine Analysis.** By J. NESSLER and M. BARTH (*Zeits. Anal. Chem.*, 21, 198).—A considerable number of analyses of wines, chiefly from the Palatinate, are given in this paper, the average of the extractives (minus acid) being, in the case of white wines, 12·8 per mille, and of red, 15·5. O. H.

**Wine made from Unripe Grapes.** By F. MUSCULUS and C. AMTHOR (*Zeits. Anal. Chem.*, 21, 192).—From the results of a number of analyses of genuine wines grown in the bad wine year 1879, the authors describe the characteristics of wine made from unripe grapes as follows:—Abnormally large amounts of extractives, acids, ash, and phosphoric acid; small proportion of alcohol, the extractives being generally of gelatinous consistency, probably due to pectinous substances.

They also find that the amount of phosphoric acid is frequently higher than the limits generally adopted for wines from ripe grapes (namely, from 0·15 to 0·18 per litre), and conclude that by far the greater proportion of mineral substances re-migrate from the fruits into the stem. O. H.

**Estimation of Glycerol in Sweet Wines.** By E. BORGMANN (*Zeits. Anal. Chem.*, 21, 239).—The author has found that while the method first proposed by Reichardt, and improved by Neubauer and himself, gives very satisfactory results in the case of dry wines, it is not applicable without modification to sweet or sugared wines, because the sugar is converted in the course of the operation into sugar-lime, which adheres so firmly to the sides of the vessels that it cannot well be removed. The author therefore operates as follows:—100 c.c. of the wine are evaporated with sand, the residue is extracted with 100 c.c. of absolute alcohol, the solution is diluted, and then well shaken with 1·5 times its bulk of ether, by which the sugar is mostly precipitated, whilst all the glycerol remains in solution; the solution is poured off, and can be treated according to Neubauer-Borgmann's method. O. H.

**Estimation of Fusel Oil in Brandy.** By L. MARQUARDT (*Ber.*, 15, 1370—1373).—The fusel oil is extracted by treating 150 grams of the brandy, diluted with an equal volume of water, with 50 c.c. of chloroform. This operation is twice repeated. The 150 c.c. of chloroform having been well washed with water to remove ethyl alcohol, are heated in a closed flask for six hours at 85°, with 5 grams of potassium dichromate, 30 grams of water, and 2 of sulphuric acid. When the oxidation is complete, the mixture is distilled, water is added to the

residue, and the distillation continued. The distillate is boiled for half-an-hour with barium carbonate, in a flask provided with an upright condenser; the chloroform is then distilled off, the residue filtered, and the filtrate evaporated to dryness. The residue is weighed, and then dissolved in water containing a few drops of nitric acid. The solution is divided into two equal portions, in one of which the barium is determined, and in the other the amount of barium chloride. The weight of barium chloride found, deducted from the weight of the residue, gives the weight of barium salts of the fatty acids. The total amount of baryta found, minus the baryta existing as barium chloride, gives the amount of baryta in these above-mentioned barium salts. If the percentage of baryta in the barium salts does not exceed 45.13 per cent., it indicates the presence of valeric acid in the oxidation-products of the chloroform extract, and hence the presence of amyl alcohol in the original brandy.

W. C. W.

**Estimation of Tartaric Acid and of Potassium Tartrate in Wine.** By C. AMTHOR (*Zeits. Anal. Chem.*, **21**, 195).—Cream of tartar and tartaric acid are usually estimated according to Berthelot and Fleurieu's method, which consists in the precipitation by ether-alcohol of the original wine, and of the wine after partial neutralisation. It is shown in the present paper that by the use of this method it not unfrequently occurs that a larger amount of cream of tartar is found than of total tartaric acid. The author finds that this is due to the precipitation by the ether-alcohol of hydrogen potassium sulphate, which is subsequently included with the tartrate. He finds that hydrogen potassium sulphate is present not only in plastered, but also in perfectly normal wines.

It is therefore inferred that Berthelot's method is not always trustworthy.

O. H.

**Testing Oil Cakes for Myronic Acid.** By V. DIRKS (*Bied. Centr.*, 1882, 487).—Ulbricht estimates the myronic acid by oxidation with bromine, but alkaline potassium permanganate will also oxidise the acid to allyl thiocyanate. By this method, 0.034–0.107 per cent. allyl thiocyanate has been obtained from pure rape seed; 0.153–0.192 per cent. from rape cake; 0.036 per cent. in turnip seed; and 1.15 per cent. in black mustard.

E. W. P.

**Estimation of Neutral Fat in Mixtures of Fatty Acids.** By M. GRÖGER (*Dingl. polyt. J.*, **244**, 303–311).—Hausaman (*ibid.*, **240**, 62) has described a method of determining undecomposed fat in mixtures of fatty acids, which the author found to give unsatisfactory results. On investigation, however, it was discovered that the failure was due to the defective description given by Hausaman, and that the method was very valuable. The author recommends the following mode of proceeding:—3 to 5 grams of the previously dried mixture of fatty acids to be examined for neutral fat are placed in a flask of 150 c.c. capacity, and dissolved completely in 25–30 c.c. of hot alcohol of about 96 per cent. Tr. After the addition of 1–2 drops of an alcoholic solution of phenolphthalein, the free fatty acid is determined by titrating the



mixture with alcoholic potash-ley (decinormal) until the red coloration ceases to disappear immediately after shaking. To determine approximately the equivalent weight of the fatty acids, a measured (excessive) quantity of alcoholic potash-ley is added, and the flask corked up. Through the cork a condensing tube 80 cm. long is passed; the mixture is then boiled for 30 minutes (if the red disappears more potash-ley is added) and titrated back with a decinormal solution of oxalic acid, until the red disappears. The precipitate of potassium oxalate produced is disregarded. This method gives accurate results only in cases where the neutral fat to be determined is the same as that from which the admixed fatty acids were separated, and provided that the saponification has extended uniformly to all the constituents of the fat. The author has therefore tried to modify this method, with the view of determining accurately the addition of a neutral fat to all fatty acids, *e.g.*, the quantity of tallow added to stearin candles, or of cocoa-nut oil present in composite candles, &c. He proceeds in the following manner:—4 to 8 grams of the fatty acids to be examined for neutral fat are dissolved in 50 c.c. of hot alcohol, about 96 per cent. Tr., a few drops of phenolphthalein are added, and the mixture is treated with decinormal alcoholic potash solution, until the red colour ceases to disappear. The whole is diluted with 150 c.c. water. Thus an alcohol of 20—25 per cent. Tr. is obtained, in which the potash soaps remain completely dissolved, but the neutral fats are insoluble. After cooling, 60—100 c.c. of ether are added; the flask is then shaken vigorously, and allowed to remain quiescent until the soap solution under the ethereal layer is perfectly clear. The solution is then drawn up with a pipette, diluted with water and heated to drive off all ether and alcohol. The fatty acids are liberated by adding dilute sulphuric or hydrochloric acid, washed with hot water until free from acid, and cooled. The equivalent weight of the carefully dried fatty acids is determined by titration with decinormal alcoholic potash-ley. The number of c.c. of alkali required to neutralise the free fatty acids in the mixture containing the neutral fat multiplied by the thousandth part of the equivalent weight found gives the weight of the fatty acids contained therein, hence the quantity of neutral fat added. The ethereal solution of the neutral fat may be used for testing the fat qualitatively.

D. B.

**Löwenthal's Method of Estimating Tannin.** By F. SIMAND (*Dingl. polyt. J.*, 244, 391—400).—The author had occasion to make a number of tannin estimations according to Löwenthal's improved method (*ibid.*, 227, 490), and found that the percentage of tannin in the same material was subject to certain variations, higher results being obtained when a larger quantity of material was boiled out. A series of experiments was therefore made, the object being to ascertain the cause of this discrepancy. The analyses were conducted in the following manner: The solution of potassium permanganate contained 1 gram per litre, 1 c.c. equal to 0.00135 g. tannin. It is standardised with iron, and the tannin equivalent calculated according to Neubauer's estimations (0.063 g. oxalic acid = 0.04157 g. tannin). The indigo solution is prepared so that 20 c.c. require 18—20 c.c. of

the solution of potassium permanganate. In titrating the tannin infusion, the author invariably used 20 c.c. of indigo solution, the advantage being that the liquid to be titrated gives the same yellow colour in each case, so that the eye gradually becomes accustomed to it. The gelatin solution is made according to Löwenthal's prescription, the filtration, however, is conducted according to Kathreiner's method (*ibid.*, 227, 481). In preparing the infusion, the quantity of tannin should be regulated so that 10 c.c. of the solution require 12 c.c. of potassium permanganate. Although it is unnecessary to adhere strictly to this strength, it is important to consider the quantity of tannin taken, and not to use too small a quantity, in which case the above-mentioned error would be multiplied. Again, it is not advisable to have the infusion in too concentrated a state, as the oxidation-products of the organic substances affect the yellow colour very considerably and hinder the recognition of the end reaction. In order to ascertain whether the extraction has been complete, ferric oxide paper is used, *i.e.*, strips of filter-paper are steeped in a solution of 1 gram ferric chloride, and 1 gram sodium acetate in 100 c.c. water, and dried in the air. This paper gives a distinctly visible black stain with a solution containing 1 part of tannin in 10,000 water. With a smaller quantity, a black ring is produced round the drop of the solution poured on filter-paper. The acidulated water used contains in 100 c.c. 3.786 g.  $\text{H}_2\text{SO}_4$ .

The analysis is made as follows: 10 c.c. of the infusion are treated in a shallow porcelain basin with 1 liter of water and 20 c.c. indigo solution. Potassium permanganate is then added slowly drop by drop until a yellow colour with faint reddish tinge is produced. To determine the oxidisable "non-tannin" constituents, the tannin in 50 c.c. of the infusion is precipitated with 50 c.c. of gelatin solution saturated with salt, and 25 c.c. acidulated water. After shaking up and allowing to stand for some time, the mixture is filtered. 25 c.c. of the clear filtrate (corresponding to 10 c.c. infusion) are then treated with 1 liter of water and 20 c.c. indigo solution, and titrated with potassium permanganate. By deducting from the quantity of potassium permanganate used in the direct titration the quantity consumed in the second titration, the number of cubic centimeters required to oxidise the tannic acid in 10 c.c. of infusion is obtained. As the volume corresponding to a certain weight of extracted material is known, and the potassium permanganate value of the tannin has been determined previously, it is easy to calculate the percentage of tannin in the tanning materials, provided that in the gelatin filtrate the "non-tannin" bodies only are titrated. This, however, was found not to be the case. The consumption of potassium permanganate in titrating the gelatin filtrate is mainly due to the solubility of the "gelatin tannate" in dilute sulphuric acid. The author is investigating this point with a view of remedying it.

D. B.

**Neubauer's Relation between the Reducing Action of Oxalic Acid and Tannin.** By C. COUNCLER and J. SCHRÖDER (*Ber.*, 15, 1373—1375).—The author finds that in their reducing action on potassium permanganate, 56 grams of iron or 63 grams of oxalic acid

are equivalent to 34.25—34.30 grams of tannin, instead of 41.2—41.57 grams of tannin, as stated by Neubauer. W. C. W.

**Reactions for Aloes.** By W. LENZ (*Zeits. Anal. Chem.*, **21**, 220—228).—Klunge states (*Schweiz. Wochenschr. f. Pharm.*, **18**, 170) that benzene extracts nothing from aqueous or alcoholic solutions of *Aloë lucida*; but that from solutions of *Aloë hepatica*, benzene, chloroform, and carbon bisulphide extract a yellow colouring matter, which becomes pink on addition of ammonia. In fairly concentrated solutions of both kinds of aloes, ferric chloride produces a brownish-black coloration. Iodine solution, added to a solution of *Aloë hepatica*, produces a beautiful reddish-violet colour, whilst it hardly affects a solution of *Aloë lucida*.

The term *Aloë hepatica* being used somewhat vaguely for any sort of liver-coloured aloes, Lenz examined undoubtedly genuine samples of aloes from Natal, Barbadoes, and Curaçoa, and of *Aloë lucida*. He found that benzene extracts from 0.3 to 3 per cent. from their aqueous solutions, and that therefore Klunge's statement is not strictly accurate.

He also investigated Bornträger's reaction (*Zeitsch. Anal. Chem.*, **19**, 165), consisting in the addition of ammonia to the benzene extract, with which it produces a reddish-violet coloration. He confirms this observation, but points out that extracts of frangula, rheum, senna, and *Spina cervina* also yield red or violet colorations closely resembling those due to aloes. These extracts also behave like aloes with iodine solution.

Whilst Klunge's and Bornträger's tests are therefore untrustworthy, Dragendorff's method was found to be perfectly satisfactory. It consists in the extraction of the fluid to be examined with amylic alcohol, which, on evaporation, leaves a residue of bitter taste, giving in solution precipitates with bromine dissolved in potassium bromide, basic lead acetate, mercurous nitrate, and tannic acid, and reducing gold and alkaline copper solution. The residue evaporated to dryness with strong nitric acid gives a blood-red coloration with potassium cyanide and hydroxide. O. H.

**The Digestibility and Quantitative Estimation of Albuminoids.** By A. STUTZER (*Bied. Centr.*, 1882, 464—467).—The author's process described in a former number (*Abstr.*, 1880, 875), is dependent on the extraction of non-albuminous matter by hot water, and the precipitation of any soluble albumin from the aqueous extract by cupric hydroxide. This method, however, requires some modification if much leucine, solanine, tannates, &c., are present also in seeds which contain much phosphates; the phosphates must be removed, otherwise cupric phosphate is formed and free alkali, the latter retaining some of the copper-albumin compound in solution. The modification is as follows: 1 gram of the substance is boiled with a mixture of 100 c.c. 95 per cent. alcohol, and 1 c.c. acetic acid, the solution after cooling is filtered, and the solid matter washed with alcohol. The residue is then heated with 100 c.c. water, allowed to cool down to 30—40°, and the dissolved albumin precipitated by

0.3—0.4 gram cupric hydroxide; after filtering, washing, and drying at 100—110°, this albumin compound is burnt with soda-lime. The quantity of soluble albumin thus obtained is to be added to that which is insoluble. To prepare the copper hydroxide, 100 grams copper sulphate are dissolved in 5 liters water to which is added 2.5 c.c. glycerol, and then sufficient sodium hydroxide to render the liquid faintly alkaline; the precipitate is to be washed with water containing 0.5 gram glycerol per litre to remove the last traces of alkali; finally the purified hydroxide is to be mixed with water containing 10 per cent. glycerol, so that all can be readily sucked up into a pipette. To prepare gastric juice solution for experimental purposes, the mucous lining of a pig's stomach is cut up in small pieces, digested with 5 litres water, and 10 c.c. of 10 per cent. hydrochloric acid for two or three days, and then the liquid is passed through flannel and filter-paper. This solution may be preserved for months if 0.5 gram salicylic acid per litre be added. Experiments with such a solution on the digestibility of the albuminoid matter in feeding cakes show that there are two classes of albuminoids present, which are chemically and physiologically different, the one "albuminoid," the other "nuclein;" the first is soluble in acid gastric juice or alkaline pancreatic juice, whilst nuclein is not; the solubility of protein is dependent on its chemical composition, that is, the amount of digestible albumin present. By artificial digestion—best by acid gastric juice—albuminous nitrogen can easily be separated from that of nuclein and determined.

E. W. P.

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## Technical Chemistry.

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**Use of Incandescent Lamps for Photographic Purposes.** By T. BOLAS (*Photographic News*, **26**, 385).—By slightly modifying an ordinary Gramme machine with 5-inch revolving armature, a 5-candle Swan incandescent lamp can be maintained at any required temperature, from a low red heat up to the point at which the filament is destroyed, affording a ready means of obtaining sufficient light to take a portrait in from 2 to 3 seconds.

To obtain this result, a small electromagnet is arranged as a keeper over the jaw pieces surrounding the revolving armature in a Gramme machine, so as to form consequent poles with those of the field magnet, the circuit being completed through the subsidiary electromagnet and the incandescent lamp. The subsidiary electromagnet placed in this position gives the machine a character intermediate between a magneto- and a dynamo-machine. When the armature is caused to rotate, and the external circuit is left open, a considerable difference of potential arises between the poles, although not so great as it would have been if the soft iron core of the electromagnet were not there acting as a

keeper to the field magnet; this potential is sufficient to insure the efficient action of the machine even when a very high resistance is included in the external circuit. When a 5-candle Swan lamp is placed in circuit, and the machine is turned with one hand at full speed, the lamp is almost immediately destroyed; but by regulating the speed any required temperature may be maintained from a low heat-heat upwards, a light of from 200 to 300 candles being readily attained. Of course the lamp is soon destroyed, but as it is used only for a few seconds each time, from 15 to 20 portraits can be taken before that occurs.

C. E. G.

**The Electric Furnace.** By C. W. SIEMENS and A. K. HUNTINGTON (*Chem. News*, 46, 163—165; *Engineer*, 54, 173).—This paper was read before Section B of the British Association at Southampton.

The furnace consists of a crucible of any convenient size, in the bottom of which is pierced a hole to receive the positive electrode, the negative electrode, which passes through a hole in the lid of the crucible, being suspended from one end of a beam, the other end of which is attached to a hollow cylinder of soft iron free to move vertically within a solenoid coil of wire. The force with which the cylinder is drawn into the coil can be counterpoised by a sliding weight on the beam. One end of the solenoid coil is connected with the positive, and the other with the negative pole. The coil having a high resistance, its attractive force on the cylinder is proportional to the electromotive force between the electrodes, *i.e.*, to the resistance of the arc. The length of the arc is therefore regulated automatically. This is a point of great importance, as, were it not so, the resistance of the arc would rapidly diminish as the temperature of the atmosphere within the crucible increased, and the result would be that heat would be developed in the dynamo-machine. The extinction of the arc by sudden change in its resistance, or by the sinking of the material in the crucible is also avoided. The crucible is surrounded with some infusible substance which is also a bad conductor of heat. Gas-retort carbon or sand answers well for the purpose. The electrodes may be of such carbon as is used in electric lighting or of any other convenient conducting substance. They may, if desired, be cooled by circulating water through or around them, or by exposing them, as far as possible, to the air. For example, in one experiment a  $\frac{1}{2}$ -inch nickel positive pole was employed, the lower end being inserted into a solid rod of copper about 1 inch square by 6 inches long. With this pole, no other means of keeping it cool being adopted, 1 lb. of grain nickel was fused in a clay crucible and poured in eight minutes, starting with all cold. The electrode was but little attacked, and no leakage occurred.

There are two great advantages possessed by the electric furnace, *viz.*, that the temperature attainable is practically limited only by the refractoriness of the materials of which the furnace is constructed, and that the heat is developed immediately in the material to be fused, instead of first having to pass through the containing vessel. On the other hand the temperature to be obtained by the use of fuel is limited by dissociation, and Deville has shown that carbonic acid

undergoes dissociation at the ordinary atmospheric pressure at about 2,600° C. Plumbago crucibles stood exceedingly well, but could not be employed where the metal was liable to be carburised. In some of the experiments, the metal was fused on a bed of lime, sand, or electric-light-carbon dust.

*Wrought Iron*.—Six pounds of wrought iron were kept under the action of the arc for 20 minutes, and the metal was then poured into a mould. It was found to be crystalline, and could not be forged.

*Steel*.—As much as 20 lb. of steel files has been melted in one charge, the time required being about one hour, starting with the furnace hot. With such large quantities, the metal has invariably been full of blowholes.

*White iron*, fused in a clay crucible for 30 minutes, when fractured did not appear to have undergone any change. White iron and coke were introduced into the furnace; the metal was found to be slightly grayer than the original. When, however, retort carbon was substituted for the coke, a good gray iron, soft and easily workable, was readily obtained in 15 minutes, starting with the crucible hot. On another occasion, starting all cold, at the end of 30 minutes, the metal, although it had been well fused, had not been rendered grayer. The difference between these two results was possibly due to the temperature being somewhat higher in the one case than in the other. This is a point of considerable practical interest. Four pounds of white iron, fused with carbon-dust for three-quarters of an hour, yielded a very gray crystalline iron.

*Cast iron*, fused and kept under the action of the arc for 45 minutes in carbon-dust, was not materially changed. Some of the same cast iron was fused for 15 minutes under lime, which nearly covered it. The character of the fracture of the metal was but little altered. A strong smell of phosphoretted hydrogen or of a phosphide was perceived in the experiment in which lime was used.

When *spiegeleisen* was fused in a plumbago or a clay crucible, graphite separated as the metal cooled.

*Siliceous pig-iron* containing about 10 per cent. silicon was fused by itself; it showed but little change, except that some graphite separated.

*Nickel*.—A positive pole of this metal—cast malleable by Wiggins and Co.'s process— $\frac{1}{2}$  inch in diameter, was passed through a hole in the bottom of a clay crucible. A carbon negative pole was used, but soon after the commencement of the experiment a deposit of nickel formed on the end of it, so that practically it was a nickel pole. This deposition of metal on the negative pole was also observed with some other metals—notably with tungsten. In the furnace arranged as just described, 1 lb. of grain nickel was fused and poured in eight minutes. The fused metal had a brilliant granular fracture. It could not be cut properly in the shaping machine, shearing off under the tool. One pound of grain nickel fused in carbon-dust for 25 minutes yielded a dark grey carburised metal, which worked well under the tool. On another occasion an equal quantity of nickel, similarly treated, gave a "blowy" metal, which could not be worked. Some carburised nickel, made as described above, was fused in a clay crucible

for 12 minutes, and allowed to cool gradually in the furnace; the fracture became whiter, and the grain closer.

*Copper*.—Three-quarters of a pound of copper were fused for about half-an-hour in carbon-dust. On examining the result, it was found that all but about  $\frac{3}{4}$  oz. had been vaporised. Those who were present during the experiments suffered no ill effects from the atmosphere charged with copper, which they must have breathed.

*Platinum*.—Eight pounds of platinum were rendered perfectly liquid in about a quarter of an hour.

*Tungsten*.—Half a pound of tungsten in powder was subjected to the action of the arc in a clay crucible. Dense fumes were evolved, and the crucible was found to have been very much attacked below the point to which the arc extended. The metal was fused only to an inappreciable depth beneath the cavity formed by the arc, but the unfused metal underneath was covered with very beautiful iridescent crystals of tungsten, which under the microscope appeared to be well-formed prisms.

A very large number of experiments were made with tungsten, the results of which showed that it could not be fused, except in very small quantities at a time. It was possible to build up a small ingot by fusing a little of the tungsten, and then adding little by little gradually. Even then the pieces were for the most part spongy and unsatisfactory. The best results were obtained when tungsten which had already been fused was employed in the building-up process. When once the metal had been fused, it did not fume much in melting, doubtless owing to the greatly reduced surface exposed.

From the foregoing experiments, it is clear that the amount of any given metal which can be successfully fused in the electric furnace, and the time required to effect the fusion, are dependent on the relation between the volatilising point and the fusing point, *i.e.*, the extent to which the volatilising point is higher than the fusing point; and on the conductivity of the metal for heat. C. E. G.

**Automatic Gas Extinguisher.** By H. MICHAELIS (*Ber.*, 15, 1397—1398).—By means of this apparatus, which resembles the ordinary alarm clock in appearance, gas taps are turned off at any desired time. The apparatus can be obtained from F. L. Löbner of Berlin. W. C. W.

**Contributions to the Study of Antiseptics.** By F. BOILLAT (*J. pr. Chem.* [2], 25, 300—309).—Koch having declared in a recent paper that most of the substances at present employed as disinfectants are practically useless, and that the only ones worthy of the name are chlorine, bromine, iodine, and corrosive sublimate, with possibly potassium permanganate and osmic acid, the author undertook the investigations recorded in this paper; he thinks that this contradiction of generally accepted facts is not as strong as it appears. As the antiseptics employed in surgery do not require to be perfect, it is sufficient for the purpose of the surgeon, if the propagation of the organisms is arrested for a time long enough to allow the wound to heal. The



spores by which some of the bacteria are propagated bear much analogy to the eggs of certain animals and the seeds of certain plants which preserve their vitality under very severe conditions, some of them not being killed even by weak acids. The classification of bacteria, according to their resistance to the action of antiseptics, has been commenced and carried to an advanced stage by Koch; the spores of the splenic fever organism preserve their vitality for many days in a 1 per cent. aqueous solution of phenol, or a 5 per cent. solution of zinc chloride, but their development is arrested; this suffices for medical purposes, as although chlorine, &c., would effectually destroy them, they would also severely injure the patient to whose wounds they might be applied.

Most antiseptics form permanent insoluble compounds with albumin, for example, egg albumin treated with a dilute solution of zinc sulphate or chloride forms Lieberkühn's zinc albuminate having the composition  $C_{72}H_{112}N_{18}SO_{22} + ZnO_2H_2$ : similar reactions occur with the other substances named by Koch, and would also occur when applied to wounds.

Samples of blood serum and egg albumin, diluted with three or four times their weight of water, were precipitated with solutions of phenol, zinc chloride, copper sulphate, corrosive sublimate, &c.—the precipitate thrown on a filter, washed until the wash-water was free from traces of the reagent, 2 or 3 grams of the damp substance was then beaten with water to a thin paste, and allowed to remain at the ordinary temperature, loosely covered with a bell-glass; watch-glasses containing serum and Koch's nutritive gelatin, without any additions, served to control the experiments, which were divided into three series—in the first the substances were left to the action of floating germs in the air. The control samples were infected in 24 hours, and became putrid in 2 to 4 days, but the other samples remained sound from 6 up to 60 days in the case of the mercury albuminate. In the second series the samples were sown with cocci, found on an infusion of coffee, and the third with splenic fever germs; in both of them the unprotected samples showed a remarkable increase of germs within the space of 2 days.

The albumin precipitated by phenol became putrid in 48 hours; the sample on being distilled with water showed no trace of phenol on adding bromine, the washing having removed it. This experiment was therefore a failure. Copper, zinc, and mercury albuminate remained for 4 weeks without perceptible change, and the author believes they would remain so for an unlimited period were oxygen and water absent.

Other experiments made with such materials as iodoform, carbon dichloride, tetrachloride, and hexachloride, solid and liquid bromotoluene, which have been favourably noticed in medical journals, were unsuccessful, and the author believes them useless as antiseptics.

J. F.

**Calcium and Sodium Glyceroborates.** By G. LE BON (*Compt. rend.*, 95, 145—146).—Calcium glyceroborate is obtained by heating together equal weights of calcium borate and glycerol at 160° with con-

stant agitation, until a drop of the liquid solidifies to a hard transparent mass on cooling. Sodium glyceroborate is obtained by heating 100 parts anhydrous borax with 150 parts glycerol. These compounds form transparent glass-like masses, which deliquesce very rapidly when exposed to the air, absorbing their own weight of water. They melt at  $150^{\circ}$ , and dissolve in half their weight of alcohol or water. Both are powerful antiseptics, have no odour, are not poisonons, and may be applied even to such a sensitive organ as the eye. Meat simply covered with a glaze of glyceroborate was sent to La Plata, and arrived in a perfectly fresh condition. From a therapeutical point of view, the sodium compound would seem to be preferable. The glyceroborates may be used in surgery in place of phenol.

C. H. B.

**Hydrogen Peroxide and its Application.** (*Dingl. polyt. J.*, **244**, 246).—After noticing the recent researches on the formation of hydrogen peroxide, the author discusses its use as a bleaching agent. According to Ebell, all materials to be bleached must be entirely freed from all fatty ingredients. For this purpose, hair is treated with a 3 per cent. solution of ammonium carbonate at  $30^{\circ}$  for 12 hours. After rinsing and washing with soap, it is treated a second time with ammonium carbonate. Feathers are cleaned with benzene or a 1 or 2 per cent. solution of ammonium carbonate and dried in the air. The bleaching is effected in a bath consisting of a 3 per cent. aqueous solution of hydrogen peroxide neutralised with ammonia. Bone, ivory, and similar substances may be treated in a like manner. It is further recommended to bleach raw silk with hydrogen peroxide.

D. B.

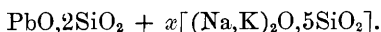
**Conversion of Waste Animal Charcoal.** By BATTUT (*Bied. Centr.*, 1882, 491).—Waste animal charcoal from sugar factories, if treated with sulphuric acid, yields a good superphosphate.

E. W. P.

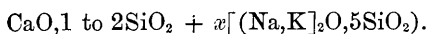
**Glass Mixtures and the Application of Natural Silicates in the Manufacture of Glass.** By G. WAGENER (*Dingl. polyt. J.*, **244**, 400—407).—In a previous paper (*ibid.*, **243**, 66, 152, and this vol., 563) the author tried to base the calculation of the ingredients necessary to form a good glass on certain rules in conformity with practical experience and the investigations of Weber on the resistance of glass. The object of the present paper is to extend these rules. In the experiments, each mixture was divided into two parts and placed in two glass pots, one being in the hottest part of a porcelain furnace, worked with a returning flame, the other in the coldest place, the object being to approximate the temperature of glass furnaces and prevent devitrification.

*Experiments with Pure Alkali Glasses.*—In both parts of the furnace mixtures of carbonated alkalis and silicic acid, corresponding with the following silicates, were introduced:— $\text{NaKO}, 5\text{SiO}_2$ ,  $\text{NaKO}, 6\text{SiO}_2$ ,  $\text{NaKO}, 7\text{SiO}_2$ ,  $\text{NaKO}, 8\text{SiO}_2$ . At the coolest part, the pentasilicate was fused to a perfectly clear mass. At the hottest part, the hex-

silicate was fused in two cases, and in a third experiment not completely. The mixture corresponding with heptasilicate was perfectly white and opaque, and the octosilicate was only sintered. Similar experiments were made with lead glass, for which the following general formula was obtained:—



Trials with calcium alkali glasses gave the formula:—



With baryta glass the following formula was obtained:—



The conclusions arrived at are these: A good glass composition must contain silica in sufficient quantity to effect the formation of the penta- or hex-silicate of the alkali and the mono-, or, better, the disilicates of the other oxides; for alumina, the tri-silicate may be taken; however, a sufficient quantity of amorphous silicates must be present to prevent devitrification. The same rules probably apply to coloured glasses, and it may be further assumed that in the above formulæ the oxides of heavy metals may be introduced in place of CaO, BaO, and PbO. Glasses used as flux presumably require other silicates than the penta- or hex-silicates. D. B.

**Influence of Sulphur and Copper on the Working Properties of Steel.** By A. WASUM (*Dingl. polyt. J.*, **244**, 456—458).—The author found that the presence of copper does not influence the malleability of steel so prejudicially as has been hitherto assumed. 0·862 per cent. copper in steel showed no traces of red shortness, the same applies to mixtures of copper and sulphur, so long as the quantity of the latter is not sufficient to render steel “red short.” With 0·107 per cent. sulphur, and 0·849 per cent. copper, the steel remained unaltered. As to the influence of sulphur on steel the author limits the quantity which renders it red short to 0·15—0·16 per cent.; he considers 0·1 per cent. injurious. D. B.

**Reduction of Silver Minerals by Hydrogen in the Wet Way.** By P. LAUR (*Compt. rend.*, **95**, 38—39).—The silver mineral (sulphide, chloride, bromide, iodide) is finely powdered and boiled in an iron vessel with a 1 per cent. solution of soda and an amalgam of 3 parts tin and 100 parts mercury. The silver is reduced and amalgamates with the mercury, the sulphur forms sodium thioannate, whilst the halogens are converted into sodium salts. There is no sensible loss of mercury. This method might probably be used with advantage on a large scale in place of the Mexican and Californian processes. C. H. B.

**Preparation of Vanadium Compounds from the Basic Slag of Creusot.** By G. WITZ and F. ASMOND (*Compt. rend.*, **95**, 42—44).—The slags produced at Creusot whilst working the Thomas-Gilchrist modification of the Bessemer process, contain as much as 1·5 per cent. of vanadium derived from the Mazenay oolite which is used in the

process, and the quantity of vanadium thus concentrated amounts to about 60,000 kilos. per annum. The roughly broken slag is treated in the cold with an insufficient quantity of hydrochloric acid until the latter is nearly saturated, and has a sp. gr. of  $36^{\circ}$  to  $27^{\circ}$  B. The solution is then decanted, diluted to  $15^{\circ}$  B., and the silica removed. This solution contains the vanadium in the hypovanadic condition, and notwithstanding the presence of foreign salts may be used with success in printing. To prepare hypovanadic phosphate, the hydrochloric acid solution is neutralised and mixed with an alkaline acetate, when a bluish-grey precipitate of hypovanadic phosphate is deposited. On repeating this treatment a precipitate is obtained which contains 20 per cent. of vanadium if the slag contained 1.5 per cent. If the slag is poorer in vanadium, the hydrochloric acid solution is neutralised by addition of powdered slag which precipitates the less soluble phosphates, including that of vanadium. This precipitate, which consists mainly of the phosphate  $(VO)_3(PO_4)_2 + 5H_2O$ , is redissolved in hydrochloric acid and then treated with an acetate, as above. The same precipitate is obtained on adding ammonium phosphate to a reduced solution of ammonium metavanadate, neutralising, and adding ammonium acetate. It is decomposed by washing, and oxidises when dried with exposure to air. These phosphatic precipitates are very soluble in acids, and have been used with success on several Indian fabrics. To prepare ammonium metavanadate, the first phosphatic precipitate, without further purification, is oxidised by roasting at incipient redness until it acquires an ochreous yellow colour. It is then treated with ammonia solution, the orange-yellow solution of ammonium orthovanadate thus obtained is boiled until colourless, filtered, and ammonium metavanadate precipitated from the filtrate in the usual way; 14 kilos. of slag containing 1.5 per cent. of vanadium gave 250 grams of almost pure ammonium metavanadate. C. H. B.

**Notes on the Manufacture of Spirit.** (*Dingl. polyt. J.*, 244, 386—391).—In discussing the determination of the refining value of crude spirit, Märker mentions that fractional distillation is the only trustworthy means of separating the impurities. Trials made to separate the bye-products by distilling over fat proved useless, whilst the use of calcium chloride did not give perfectly pure ethyl alcohol. With Savalle's diaphanometer the value of crude spirit may be determined approximately. The apparatus is based on the fact that pure ethyl alcohol is not coloured when boiled with sulphuric acid, whilst the impurities give a yellow or brown colour, the quantity varying with the intensity of the colour, so that by comparison with a certain scale the purity of a spirit may be roughly estimated. Pampe finds that the physical miscibility of the impurities with ethyl alcohol is of great importance. Aldehyde, *e.g.*, is miscible with ethyl alcohol almost in all proportions, and therefore considerably reduces the value of crude spirit, whilst amyl alcohol is easily separated. Potato spirit, which contains chiefly amyl alcohol, is therefore more valuable than spirit made from maize or molasses. According to Märker, grain spirit should be prepared exclusively from rye, maize being regarded as an adulterant. Delbrück describes some improvements made in apparatus

for distilling mash and for rectifying, consisting essentially in a reduction of time and in working the stills uninterruptedly. Cast-iron stills are said to answer very well; it is necessary, however, to see that the steam in entering the still does not play directly on the sides or bottom, as the protecting layer of graphite would thus be removed. Petzold has made some experiments on saccharification with malt. He finds that with malt extract previously heated to  $61^{\circ}$ , 30 to 40 per cent. less sugar is formed than in the usual manner of conversion. At a temperature of  $50^{\circ}$  the difference is small, so that the injurious action may be said to begin at this temperature. It is further mentioned that the result is not altered when the malt extract is added in one portion to the starch, or gradually. Franke finds that by steaming the mash for a long period the quantity of sugar is increased but the yield of spirit diminished. D. B.

**Plastered Wines.** By M. NENCKI (*J. pr. Chem.* [2], 25, 284—299).—The Government of the Canton of Berne having passed a law forbidding the sale of wines containing more than 2 grams of potassium sulphate to the litre, wine merchants complained of the severity of the regulation, and the Government appointed a Commission to investigate the subject; the author was the reporter, and gives the results of their investigations. Their opinions were invited as to whether the use of wine containing more than the legal limit of the sulphate is injurious to health; whether the limit could safely be extended, and to what extent; and whether there is any difference between the effects of plastered white and red wines.

The public opinion is strongly against the custom: Spanish, Italian, and South of France wines are those most generally clarified with gypsum; it is said to increase the quantity, improve the colour, and raise the alcoholic strength, thereby improving the keeping qualities; it is also said to prevent after-fermentation; but its real advantage to the wine maker is that it clarifies the wine rapidly and allows it to be quickly brought to market. It is chiefly employed with the coarser qualities of red wine, and is either added to the grapes and trodden with them, or in fewer cases added to the expressed juice; the quantity used is generally 1—2 kilos. to every 100 kilos. of fruit; but it is sometimes as much as 10 kilos.

The most exhaustive inquiry yet made on the subject was by a Commission appointed by the French War Department, and the conclusions arrived at by them have been confirmed and fully adopted by the author and his colleagues, they are:—

The addition of gypsum to wine cannot be detected by the flavour, but it lessens the intensity of the colour; it decomposes the acid potassium tartrate naturally present in the wine, potassium sulphate remaining in solution and the tartaric acid uniting with the lime to form an insoluble calcium tartrate. Potassium phosphate, also a natural constituent of wine, is decomposed, forming potassium sulphate and insoluble calcium phosphate. It is a debatable question whether the potassium tartrate naturally existing in wine is the acid or neutral salt, and, considering that there are also present succinic, malic, and various volatile fatty acids, and that the gypsum itself contains varying

proportions of carbonate, it is difficult to understand the reactions; but, as the natural acidity of wine is more than sufficient to transform all neutral into acid salts, the author is of opinion that it is the acid tartrate which is present. It would also appear that some free sulphuric acid is formed in the plastered wine, as, when it is left for a certain time, ethyl ether is produced,—at least such was the result of one experiment made by the author.

Although much has been said as to the toxical effects of plastered wine, very few trustworthy examples have been recorded. The first complaints were made by the French army in Africa, where many cases of illness were said to be caused by its use. The only other attested case is that of an epidemic which broke out in the Department of the Loire, but alum was found to have been added to the wine as well as gypsum. The symptoms are said to be colic and slight vomiting. The acid potassium tartrate acts towards many reagents in the same manner as free sulphuric acid, and when introduced into the system may have the effect of reducing the alkalinity of the blood.

In view of the inconclusive nature of the evidence, the Commission recommend the maintenance of the regulation forbidding the sale of wines containing more than 2 grams of potassium sulphate in the litre.

J. F.

**Presence of a Glycol in Wine.** By A. HENNINGER (*Compt. rend.*, 95, 94—96).—By careful fractionation of 50 litres of red Bordeaux wine, with the aid of Le Bel-Henninger tubes, the author has succeeded in isolating about 6 grams of isobutyl-glycol, b. p. 178·5°. Making a correction for the glycol carried away by the aqueous vapour, the amount of glycol present in the wine is about 0·05 per cent., or about one-fifteenth the amount of the glycerol present.

C. H. B.

**Preparation of Pressed Yeast.** (*Dingl. polyt. J.*, 244, 448—456).—Hayduck has investigated the utilisation of the nitrogenous constituents in the manufacture of pressed yeast. To determine the quantity of nitrogen contained in the raw materials, which can be assimilated by the yeast, the finely bruised substances were extracted with distilled water at 50°, or with dilute sulphuric acid at the same temperature. The total quantity of soluble proteids was determined in the filtrate, after which the solution was treated with a sufficient quantity of sugar. Seed-yeast was then added, and the nitrogen was again determined after the end of the development. The difference between the nitrogen obtained and the total quantity originally found in the solution, gives the nitrogen assimilated by the yeast. From oats, about 38 per cent. proteids could be extracted with water at 50°; the quantity of assimilable proteids, however, was only about 16 per cent., so that it was impossible to draw any conclusions from these data as to the utility of the solution in the nutrition of yeast. Maize lost about 12 per cent. of soluble proteids, of which 7 per cent. was assimilable. Hence, maize protein is less soluble in water than the proteids of oats, but a larger proportion of the former is utilised in the nutrition of yeast. From oats treated with water and lactic acid (0·5 per cent. solution), 60 per cent. of proteids was dissolved, 31 per

cent. being assimilable. Lactic acid has a powerful peptonising action on oat protein, but with maize it seems to be without action. In the case of barley-malt, large quantities of proteids were dissolved by the treatment with water and  $\frac{1}{2}$  per cent. lactic acid. In another experiment, malt and potatoes were mashed together in the proportion of 1 : 24, and the mixture diluted to 12° saccharometer. On analysis, the potato-mash gave 0.1 per cent. dissolved nitrogen; 60 per cent. being assimilable. It is shown that, contrary to the opinion usually held, this solution is well adapted to the growth of yeast.

Delbrück describes the employment of potatoes in the cultivation of pressed yeast. According to the process of Schuster and Burow, the potatoes are steamed, water being previously added. Schuster further uses a small quantity of sulphuric acid. The pressure is maintained at a moderate degree. Burow recommends to introduce into the steamers first the potatoes, then the necessary quantity of water, and finally the requisite quantity of bruised maize. The effect of the addition of a small amount of sulphuric acid is not only to improve the colour, but to prevent the formation of bacteria.

Birner recommends the use of asparagine as nutriment for the yeast cell; for this purpose leguminous seeds are steamed and added to the mash.

Schuster proposes to prepare pressed yeast and spirit from unbruised corn without the application of steam pressure. The corn is digested with sulphuric acid at 46° (100 kilos. corn, 660 c.c. pure sulphuric acid, and 200 litres water). After the expiration of 48 to 60 hours, the material is brought into a mashing vat and ground to a fine powder, which is effected with great ease. The saccharification is more rapid and complete.

Hayduck has studied the influence of alcohol on the development of yeast. Fusel oil was found to retard considerably the progress of the fermentation of yeast. 0.5 per cent. amyl alcohol in a 10 per cent. solution of sugar impeded its progress, while 2 per cent. completely prevented the fermentation. Alcohol arrests the fermentation if present to the extent of 15 per cent. by volume, and smaller quantities retard the action. The fact that the formation of yeast is usually completed after the expiration of about 30 hours is explained either by the consumption of an ingredient in the mash indispensable to the development of yeast, or by the formation of a fermentation product which prevents the further progress of the yeast. It was also found that a solution of potato-mash containing 9.25 per cent. (by volume) of alcohol showed signs of fermentation after filtration and addition of yeast, but did not develop yeast. After the removal of alcohol from another portion of the filtrate by distillation, adding water to make up the solution to the original volume, and treatment with yeast, a further growth occurred with consumption of nitrogenous constituents. In conclusion, it is mentioned that the assumption that potato-mash is deficient in nitrogenous nutrients is disproved by these experiments.

D. B.

**Xylidine-Ponceau.** By E. BLONDEL (*Dingl. polyt. J.*, **244**, 458).—The ponceau introduced by Poirrier in September, 1879, is obtained

by the action of a dilute solution of a salt of diazoxylene on naphthol-disulphonic acid; the solution is rendered alkaline, and the colouring matter precipitated with common salt. It is readily soluble in water and acetic acid, but less so in alcohol or glycerol. It has no affinity for vegetable fibres, but dyes animal fibres without a mordant. The colour resists the action of light, but does not stand soaping. Although fast in the air, the ponceau fades slowly on exposure to direct sunshine. Tannin, vegetable colouring matters, gum, starch, dilute sulphuric acid and hydrochloric acid do not act on it. It is precipitated from its solution by the acetates of lead and aluminium in the form of a lake; barium salts precipitate it more readily, and the addition of acetic or hydrochloric acid does not affect the lake produced. Like the aniline colours, the ponceau is frequently adulterated with dextrin. By washing the colouring matter with a sufficient quantity of alcohol, which dissolves the ponceau, the impurities such as dextrin, &c., remain behind. D. B.

**Application of Alizarin in Dyeing and Calico Printing.** By G. STEIN (*Dingl. polyt. J.*, **244**, 311—321).—Alizarin is principally distinguished as yellow shade and blue shade alizarin, whereas the former contains a large proportion of flavo- or anthra-purpurin, the latter consists mainly of alizarin. It is fixed on the fibre for red with aluminium mordant, for purple with iron, and for brown with chromic oxide. Nitroalizarin gives an orange colour with aluminium salts, whilst cachou colours are produced with chromium mordants. Alizarin blue is always fixed with the latter mordant. For dyeing and printing with alizarin, it is essential to bleach the goods as white as possible.

*Alizarin for Red Prints.*—The well bleached cotton is passed through a bath consisting of a solution or decoction of Turkey-red oil (sulphoricinoleic acid) in distilled water in the proportion of 1 : 10, 15, 25 or 50, the quantity being determined by a preliminary dye-test. The aged goods are dried on metal cylinders, and the steam colours for red or pink printed on. As fixing agents, aluminium acetate or nitrate is used. The following mixture is boiled in copper or tin boilers.

*Alizarin Red I.*—750 grams wheat starch, 4700 water, 570 alizarin yellow shade, 20 per cent. paste, 750 alizarin blue shade, 20 per cent. paste, 400 calcium acetate of 15° B., 1000 acetic acid of 6° B., and 580 tragacanth mucilage  $\frac{1}{2}$ . 800 grams olive oil are then added, and the mixture is allowed to cool. Before printing, it is treated with 540 grams aluminium acetate of 12° B., 360 aluminium nitrate of 15° B., 13 stannic oxalate, and made up to 10,000 grams with water. The following mixture is prepared in the cold.

*Alizarin Red II.*—6700 grams starch-tragacanth thickening, 1200 alizarin yellow shade, 20 per cent., 400 calcium acetate of 15° B., 800 olive oil, and 900 aluminium sulphocyanate of 19° B.

*Alizarin Pink A.*—7800 grams starch-tragacanth thickening, 430 alizarin blue shade, 20 per cent., 444 water, 156 calcium acetate of 15° B., 263 olive oil, 312 aluminium acetate of 12° B., 166 tin oxalate, and 429 acetic acid of 6° B. Recently the three last-named substances have been replaced by 312 grams aluminium thiocyanate of 19° B., and



595 water. The prints are dried and passed through the English aniline fixing apparatus for one minute. The pieces are then steamed for an hour and cleared. For this purpose, various processes are in use, such as passing the fabric through a hot chalk bath, washing and soaping or subjecting it to a chlorine steaming apparatus, and then soaping. In some works, the goods are cleared after these operations in a closed boiler under pressure in a mixture of 28 grams tin salts, 45 crystallised sodium carbonate, 7 litres thin soap solution made up with water to 200 litres. As reserve, zinc sulphate or chromium tartrate is used.

*Reserve I.*—1104 grams zinc sulphate are dissolved in 828 water treated with 70 soda-lye of 36° B., diluted with 130 water and 7895 gum water  $\frac{1}{4}$ .

*Alizarin for Red Dyeing.*—The main differences are of a mechanical nature. In some works hot flues, in others printing machines, are used. In the first case, the white goods are prepared with Turkey-red oil (1 : 15, 20 or 25) dried and oxidised, then washed and dried. The pieces are now passed through a hot flue, a mordant 3° to 5° B. in strength being printed on. This is formed by the double decomposition of equal parts of lead and aluminium pyrolignite. After drying, the goods are hung up in a moist warm atmosphere (28—33°) or passed through an oxidation chamber (43°). After being drawn through a bath of cowdung and chalk at 63—75°, and washed, they are ready for dyeing. According to the second method, the goods prepared with Turkey-red oil are blocked in the printing machine. The mordant in this case requires a thickening agent, the following mixture being used:—320 grams wheat starch, 320 flour, 400 burnt starch water (750 grams per litre), 160 olive oil, 2730 aluminium pyrolignite of 12.5° B., and 5960 water, are boiled and stirred until cold. Before blocking, 40 grams fused tin chloride of 66° B., and 70 magenta solution (4 grams per litre) are added. After drying and oxidation, the goods are passed through a bath of soluble glass, chalk and cowdung, washed, dunged a second time, again washed with water, and dyed. For 120 m. cloth 80 cm. wide about 1 kilo. alizarin 20 per cent. paste is used. After dyeing, the pieces are washed, dried, oiled, steamed under pressure for one hour, and finally soaped. The following are receipts for purple, violet, black, orange, and blue alizarin:—

*Alizarin Purple B.*—1200 grams alizarin 20 per cent. blue shade, 1200 water, 800 acetic acid of 6° B., 600 calcium acetate of 15° B., 1000 iron pyrolignite of 11° B., and 5600 thickening.

*Violet 7.*—6125 grams burnt starch water (dark), 372 pyroligneous acid of 4° B., 387 iron pyrolignite of 10° B., 1634 burnt starch water (light) are mixed with 39 grams slaked lime, 279 arsenious acid, 243 copper sulphate, and 921 water.

*Black 8.*—2766 grams iron pyrolignite of 10° B., 2766 logwood extract of 10° B., 645 water, 1344 acetic acid of 6° B., 2904 burnt starch are made up to 10,000 grams with water after boiling.

*Brown C.*—10,000 grams steam alizarin red colour, 200 extract of buckthorn berries, 200 red potassium prussiate; and for *Brown B*, 1200 grams alizarin 20 per cent. blue shade, 1200 chromium acetate of

18° B., 300 crystallised barium acetate, 1300 water, and 6000 thickening.

*Orange*.—7096 grams thickening, 1740 nitroalizarin 15 per cent., 814 aluminium nitrate of 15° B., 350 calcium acetate of 10° B.

*Blue*.—5640 grams thickening, 2820 alizarin blue 10 per cent., 630 chromium acetate of 16° B., and 910 magnesium nitrate of 15° B.  
D. B.

**Presence of Nicotine in Tobacco Smoke, and Consideration of the Active Poison in the Combustion-products of Tobacco.** By R. KISSLING (*Dingl. polyt. J.*, **244**, 234—246).—Having discussed in a previous paper the principal publications on this subject (this vol., 906), the author proceeds to give an account of his own investigations on the composition of tobacco smoke, mainly with a view of proving the presence of nicotine. His experiments were made with cigar smoke, as this is the form in which tobacco is most extensively consumed, the prevailing conditions being less complicated than the smoking of tobacco from pipes of various shapes. The smoke of a cigar was drawn by means of an aspirator through a long condensing tube and a system of five flasks. The first and third flasks were empty, the second contained alcohol, the fourth dilute sulphuric acid, and the fifth weak soda-lye. The current of air, and with it the intensity of smoking, was regulated so that a cigar lasted for about half an hour. The ingredients condensed and absorbed in the various flasks were then examined.

Full details are given of the various experiments and of the methods of examination employed, the results being arranged in a series of tables.

In discussing these results, the author mentions that, although the presence of nicotine in tobacco smoke can be detected qualitatively with great ease, it is difficult—in fact it seems impossible—to effect an approximate separation of nicotine from the condensation-products of the smoke. Without wishing to dispute the assumption that the various basic substances formed by the combustion of tobacco are comparatively numerous, the author is led to conclude from the properties exhibited by the basic mixtures he has isolated, that besides nicotine they contain in appreciable quantity only the lower members of the picoline series. As the difference in the boiling points between the picoline bases and nicotine increases, the platinum in their platinochlorides approaches that of nicotine platinochloride, so that by determining simultaneously both these points it was possible to ascertain with some degree of certainty the existence of a considerable contamination of the nicotine with picoline bases. The following are the boiling points and the percentage of platinum in the platinochlorides:—

	Boiling point.	Percentage of platinum.
Pyridine .....	115°	34·68
Picoline .....	135	33·05
Lutidine .....	155	31·58
Collidine .....	171	30·23
Parvoline .....	188	29·00
Coridine .....	211	27·84
Rubidine .....	230	26·82
Vividine .....	251	25·81
Nicotine .....	242	34·36

The quantities of nicotine given in Table A were calculated in the following manner:—As the boiling points of the isolated nitrogenous bases (with one exception) were always above 200°, the percentage of their platinochlorides formed the essential point of deciding their constitution. When below 34·15 per cent., the corresponding numbers were calculated as pure nicotine; the same applied to those cases where the percentage of platinum was higher than 34·5, as here probably a partial separation of metallic platinum, caused by the presence of a small quantity of pyrroline, had occurred. An extreme case (35·51 per cent. Pt) was obtained in experiment 3, in which unquestionable contamination with metallic platinum had taken place; 80 per cent. of the nitrogenous bases obtained was calculated as nicotine. When the percentage was below 33·7 the corresponding numbers were disregarded. In cases where the values were within 34·15 and 33·90 per cent. and 33·90 and 33·70 per cent., 90 and 80 per cent. of the corresponding nitrogenous bases were relatively calculated as nicotine. In experiment 4 the basic mixture began to boil at 130°, whilst the percentage of platinum in the platinochloride was 34·13 per cent. It must therefore be assumed that the mixture was contaminated more largely with the lower-boiling picoline bases: hence only 80 per cent. of the corresponding nitrogenous bases has been calculated as nicotine. With the numbers thus obtained the following values were calculated:—

Table A.	Experiment 1.		Experiment 2.		Experiment 3.		Experiment 4.		Experiment 5.	
	grams.	p. c.	grams.	p. c.	grams.	p. c.	grams.	p. c.	grams.	p. c.
Tobacco used.....	406·675	..	341·60	..	798·00	..	513·00	..	..	..
Per cent. nicotine.....	..	3·75	..	3·75	..	0·30	..	0·19	..	2·24
Total nicotine.....	12·250	..	12·810	..	2·394	..	0·975	..	..	..
Tobacco smoked.....	350·42	..	216·60	..	700·00	..	441·00	..	..	..
Nicotine smoked.....	13·141	..	8·123	..	2·100	..	0·838	..	..	..
Nicotine obtained from the smoke.....	6·836	..	2·261	..	1·769	..	0·588	..	..	..
The same calculated on smoked nicotine...	..	52·02	..	27·83	..	84·23	..	70·16	..	..
The same calculated on total nicotine.....	..	44·83	..	17·65	..	73·89	..	60·32	..	..
Tobacco not smoked.....	56·255	..	125·00	..	98·00	..	72·00	..	250·00	..
The same calculated on total tobacco.....	..	13·83	..	36·59	..	12·28	..	14·03	..	..
Nicotine obtained from tobacco not smoked	2·832	..	5·640	..	..	..	..	..	6·278	..
The same calculated on tobacco not smoked	..	5·03	..	4·51	..	..	..	..	..	2·51
The same calculated on total nicotine.....	..	18·57	..	44·03	..	..	..	..	..	..
Decomposed nicotine.....	5·582	..	4·909	..	..	..	..	..	..	..
The same calculated on total nicotine.....	..	36·60	..	38·32	..	..	..	..	..	..

The conclusions arrived at by the author may be summarised as follows:—Carbonic oxide, sulphuretted hydrogen, hydrocyanic acid, the picoline bases, and nicotine are the active poisons contained in tobacco smoke. The quantity of the first three constituents, however, is too small, and their volatility too great to be of importance in determining the influence of smoking on the organism. The picoline bases also are present in relatively small quantities, so that the toxic action of the smoke is essentially due to the large proportion of nicotine contained therein. Of the total nicotine contained in a cigar the proportion destroyed by the combustion process is very small. D. B.

**Reducing Action of Glycerol on Silver Salts, and its Application to Silvering Glass.** By G. PALMIERI (*Gazzetta*, 12, 206—209).—After noticing the methods proposed for forming a silver mirror on glass, the author gives the results of his own experiments. If glycerol is added to an ammoniacal solution of silver nitrate, it becomes brown after a time, and gradually deposits a black substance; this action is greatly accelerated by heating the solution, a portion of the silver being deposited as a steel-grey mirror. If a few drops of potash solution are added to the mixture of glycerol and ammoniacal silver, a brilliant mirror is soon formed on the interior of the vessel. The phenomenon is even more striking if the ammoniacal silver solution be first mixed with potash, and glycerol then added: directly the glycerol comes in contact with the silver solution, reduction takes place with formation of a brilliant metallic mirror. If ether is added to the mixture of glycerol, potash, and ammoniacal silver nitrate, as soon as it touches the aqueous liquid, a metallic ring is formed at the junction of the two liquids, and in a few seconds reduction is complete through the whole bulk of liquid. If alcohol is added to the glycerol-silver mixture, reduction is somewhat accelerated, and the metallic mirror is always brilliant.

The results of these experiments show that the reducing action of glycerol on silver salts may be applied technically with advantage to silvering mirrors, both from the facility with which the process may be conducted, and from its economy. The author promises details in a future communication. C. E. G.

**Product of the Distillation of Beet-molasses Waste.** By C. LAUTH (*Bied. Centr.*, 1882, 485).—The residue of sp. gr. 4° B. is evaporated to about 37° B., and then submitted to distillation in iron retorts; a mixture of coke and salt is left in the retorts; one day's working gave the following results:—400,000 kilos. waste gave 10,000 kilos. potashes, 1600 kilos. ammonium sulphate, 100 kilos. methyl alcohol, and 1800 kilos. concentrated mother-liquor, containing salts of trimethylamine. The 4000 kilos. tar which was obtained yielded 360 kilos. oil, 2000 kilos. ammoniacal water, and 1600 kilos. asphalt.

E. W. P.

## General and Physical Chemistry.

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**Chemical Work done by the Galvanic Cell.** By D. TOMMASI (*Compt. rend.*, **95**, 174—177).—A zinc platinum couple immersed in chromic acid solution can effect exterior chemical decomposition equivalent to only 65 cal.; but if carbon is substituted for the platinum, the couple can effect decomposition equivalent to more than 82 but less than 90 cal. The electromotive force of a zinc and spongy platinum couple in chromic acid is greater than that of a zinc and sheet platinum couple, and approaches that of the zinc carbon couple; hence it would appear that the physical condition of the platinum exerts considerable influence on the electromotive force of the couple. C. H. B.

**Variation in Friction produced by Electrical Polarisation.** By KROUCKOLL (*Compt. rend.*, **95**, 177—178).—The author finds that polarisation by oxygen increases the friction between glass and platinum, whilst polarisation by hydrogen diminishes the friction. The increase or diminution of the friction increases with the electromotive force which produces polarisation. C. H. B.

**Numerical Relations between Thermo-chemical Data.** By D. TOMMASI (*Compt. rend.*, **95**, 287—290).—The author enunciates the following law:—*When a metal displaces another metal in a saline solution, the quantity of heat developed is always the same for each metal, whatever the nature of the acid radicle in the salt or of the haloïd with which the second metal is combined.* For example, when zinc displaces copper in copper sulphate, 50·6 cal. are developed; and the same quantity of heat is developed when zinc displaces copper in any copper salt. The author has drawn up a table of the thermal constants of the substitution of potassium for other metals in saline solutions. From the numbers given, it is possible to calculate the heat of formation of any particular salt of the 18 metals given in the table with the aid of the formula  $\Delta = \delta \pm \theta$ , in which  $\Delta$  is the heat of formation of the given salt,  $\delta$  the heat of formation of the potassium salt having the same acid radicle as the salt  $\Delta$ , and  $\theta$  the thermal constant corresponding to the base of the salt  $\Delta$ . The numbers thus calculated agree very closely with those obtained by experiment. C. H. B.

**Heat of Solution of some Mixtures of Salts.** By P. CHROUSTCHOFF (*Compt. rend.*, **95**, 221—223).—The author has determined the heat of solution at 12° of a mixture of 2 mols. potassium chloride with 1 mol. ammonium sulphate, and of a mixture of 2 mols. ammonium chloride with 1 mol. potassium sulphate, with the following results:—

First system.....  $2\text{KCl} + (\text{NH}_4)_2\text{SO}_4 - 12\cdot76$  cal.  
 Second system....  $2\text{NH}_4\text{Cl} + \text{K}_2\text{SO}_4 - 15\cdot51$  „

In both cases, the number obtained is slightly higher than the sum of the heats of solution of each salt taken separately. The solutions were evaporated to dryness (1) at  $100^\circ$ , (2) over sulphuric acid in a vacuum at the ordinary temperature, and the heats of solution of the residues were determined.

	1.	2.
First system .....	13·70	13·65
Second system .....	13·94	13·92

It is evident, therefore, that no initial systems exist in solutions of mixtures containing ammonium salts. The complex equilibrium observed in certain cases depends entirely, as Berthelot has shown, on the degree of dissociation of the ammonium salts under the conditions of the experiment. The results obtained by the author with ammonium sulphate do not agree with those obtained with the nitrate by Rüdorff, who found that evaporation at  $100^\circ$  gave a system of four salts, whilst evaporation in the cold always gave the same system of two salts, whatever the initial system.

The author has also determined the heats of solution of fused mixtures of two salts, and concludes that when two salts are fused together there is no division of the acids, but a system of two salts is formed in accordance with Berthelot's law. C. H. B.

**Heat of Formation of Palladious Compounds.** By JOANNIS (*Compt. rend.*, **95**, 295—297).—The author has obtained the following results:—

$\text{Pd} + \text{Br}_2$ liquid = $\text{PdBr}_2$ solid .....	+ 24·88
„ „ „ gas = „ „ .....	+ 32·88
$\text{PdBr}_2$ solid + $2\text{KBr}$ dissolved = $\text{PdBr}_2\cdot 2\text{KBr}$ solid ..	+ 15·32
„ „ „ „ dissolved .....	+ 2·84
$\text{Pd} + \text{O} = \text{PdO}$ precipitated .....	+ 20·0
$\text{Pd} + \text{Cy}_2$ gas = $\text{PdCy}_2$ precipitated .....	+ 23·6
$\text{Pd} + \text{I}_2$ solid = $\text{PdI}_2$ precipitated .....	+ 13·4
„ + „ gas = „ „ .....	+ 24·0
$\text{Pd} + \text{Cl}_2 = \text{PdCl}_2$ solid .....	+ 40·48
$\text{PdCl}_2$ solid + $2\text{KCl}$ dissolved = $\text{PdCl}_2\cdot 2\text{KCl}$ solid ..	+ 9·32
„ „ „ „ dissolved .....	+ 4·72

From these numbers it follows that—

	Cals.
$\text{PdO}$ precip. + $2\text{HCl}$ dilute = $\text{PdCl}_2$ precip. + $\text{H}_2\text{O}$ , develops +	10·8
„ „ + $2\text{HBr}$ „ = $\text{PdBr}_2$ „ „ „	+ 14·8
„ „ + $2\text{HI}$ „ = $\text{PdI}_2$ „ „ „	+ 35·8
„ „ + $2\text{HCy}$ „ = $\text{PdCy}_2$ „ „ „	+ 44·8

Hydrocyanic acid displaces all the other hydracids and decomposes the chloride, bromide, and even the iodide.

Potassium palladiochloride crystallises in slender needles belonging to the quadratic system. The crystals are a combination of the prism

with the octohedron, the angles of the prism being  $mm$   $90.02^\circ$ ,  $mb_1$   $120.25^\circ$ , and  $b_1 b_1$   $137.54^\circ$ . Potassium palladiobromide forms large crystals belonging to the rhombic system. Sometimes they show macles resembling those of staurolite. The crystals are combinations of the prism  $p$  and the faces of the octohedron  $b_1 b'_1$ , the angles being  $pb_1$   $121.07^\circ$ ,  $pb'_1$   $125.23^\circ$ ,  $b'_1 b_1$   $117.44^\circ$ .  
C. H. B.

**Specific Volumes of Liquids.** By A. ZANDER (*Ber.*, **15**, 1430—1431).—The results described in the author's dissertation (Königsberg) agree with those independently and contemporaneously obtained by R. Schiff (*Ber.*, **15**, 1270).  
W. C. W.

**Molecular Volumes of the Alums.** By O. PETTERSSON (*Ber.*, **15**, 1739—1741).—The author criticises Spring's law (*Ber.*, **15**, 1254), "that under similar physical conditions equal volumes of isomorphous bodies contain the same number of molecules," and points out that rubidium alum has the sp. gr. 1.890 at  $20^\circ$ , and the molecular volume 551.1, whereas potassium alum has the sp. gr. 1.7538 and the molecular volume 541.2.  
W. C. W.

**Elasticity of Rarefied Gases.** By E. H. AMAGAT (*Compt. rend.*, **95**, 281—284).—The author has repeated his experiments (*Ann. Chem. Phys.* **8**), with improved apparatus and under very low pressures, and concludes that gases obey Boyle's law even under pressures of less than a millimetre. The errors of observation are, however, so large compared with the differences to be observed, that no very definite conclusions can be drawn.  
C. H. B.

**Influence of the Quantity of Gas Dissolved in a Liquid on the Surface-Tension of the Latter.** By S. WROBLEWSKI (*Compt. rend.*, **95**, 284—287).—The author arrives at the following conclusions:—Under pressures of from 1 to 30 atmospheres there is an intimate relation between the law of solubility of carbonic anhydride in water, and the surface-tension of the latter. The product of the surface-tension  $\alpha$  into the pressure  $P$ , to which the carbonic anhydride is subjected, is proportional to the coefficient of saturation  $S$ , which corresponds with that pressure; in other words  $\alpha P = AS$ , where  $A$  is a coefficient which increases with the temperature. According to the first law of solubility, the temperature being constant,  $\frac{S}{P}$  diminishes as the pressure increases (*Compt. rend.*, **94**, 1355). Experiment shows that the diminution of  $\alpha$  is proportional to the diminution of  $\frac{S}{P}$ . The pressure being constant and equal to  $n$  atmospheres, where  $n$  is greater than 1, it follows from the laws of solubility that the quotient—

$$\frac{\left(\frac{S}{P}\right)_{P=n}}{\left(\frac{S}{P}\right)_{P=1}}$$

diminishes with decrease of temperature. Experiment shows that the



ratio of the surface-tensions corresponding with the pressures  $\frac{\alpha_p = n}{\alpha_p = 1}$  also decreases under the same conditions.

These conclusions do not agree with Kundt's theory that the surface-tension is directly affected by the pressure. As a matter of fact the variation in the surface-tension is independent of the pressure, and depends only on the amount of gas dissolved in the superficial layer of the liquid. The solubility of carbonic anhydride in water increases less rapidly than the pressure, and tends towards a limit which is apparently reached when the carbonic anhydride liquefies, since the liquid does not mix with water. The diminution of the surface-tension also decreases as the pressure rises, and tends towards a limit which, at  $0^\circ$ , is reached when the pressure is sufficient to liquefy the carbonic anhydride. At this point the surface-tension of the water is reduced by one-half.

Carbon bisulphide behaves in a similar manner. The decrease in the surface-tension takes place much more quickly at  $0^\circ$  than at a higher temperature, but becomes less rapid, and finally stops when the gas liquefies. If, however, the liquid used will mix with liquefied carbonic anhydride, the phenomena observed are different. They will be described in a subsequent paper.

C. H. B.

### **Congelation of Solutions of Neutral Compounds in Benzene.**

By F. M. RAOULT (*Compt. rend.*, **95**, 187—189).—The author has determined the reduction of the freezing point of benzene caused by dissolving in the latter a number of organic substances. He finds that ketones, aldehydes, ethers, hydrocarbons, and their derivatives, dissolved in the same weight of benzene in quantities proportional to their molecular weights, lower the freezing point of the benzene by the same amount. The product of the molecular weight of the substance into the reduction of the temperature produced by 1 gram is approximately 50. Combining these results with those previously obtained with water, the author concludes that *in a large number of cases the reduction of the freezing point of a solvent by a substance dissolved in it depends only on the relation between the number of molecules of the solvent and the substance dissolved, and is independent of the nature, the number, and the arrangement of the atoms of which the dissolved molecules are composed.*

C. H. B.

**Propagation of Explosions in Gases.** By BERTHELOT and VIEILLE (*Compt. rend.*, **95**, 151—157).—The authors have previously shown (this vol., 685) that an explosion is propagated in gaseous mixtures in the form of a wave, and that the rapidity of propagation is, within certain limits, independent of the pressure and of the diameter of the tube. Further experiments with mixtures of oxygen or nitrous oxide with hydrogen, hydrocarbons, and cyanogen, have shown that the velocities calculated by means of Clausius's formula agree approximately with those actually observed, but are somewhat too high, the differences between the observed and calculated values varying from 5 to 12 per cent. This holds good whatever the relative proportions of the mixed gases and the degree of condensation. With

mixtures of oxygen or nitrous oxide with carbonic oxide, however, the difference between the observed and calculated velocity is as much as 40 per cent. The velocity of propagation in isomeric mixtures, *i.e.*, mixtures which yield the same final system after explosion, is approximately the same. If the explosive mixture is mixed with some inert gas, the observed velocity of propagation is considerably lower than the calculated value. When the composition of the gaseous mixture approaches the limit at which the explosion is not propagated, the velocity of propagation is considerably diminished. C. H. B.

**Detonation and the Production of an Explosive Wave.** By BERTHELOT and VIEILLE (*Compt. rend.*, 95, 199—205).—The propagation of an explosive wave is a phenomenon altogether distinct from ordinary combustion, and takes place only when the ignited stratum of gas exerts the greatest possible pressure on the adjacent stratum, that is, when the inflamed molecules possess the maximum force of translation, or in other words, when the molecules retain almost the whole of the heat developed by the chemical reaction. It must be borne in mind, however, that it is the wave, and not the mass of gas, which is transmitted. Dissociation apparently plays little part in the phenomenon, probably on account of its short duration. The velocity with which the wave is transmitted is the same whether the tube is open at both ends, closed at one end, or closed at both ends. The velocity and pressure are intimately connected, any increase of pressure being attended by increased velocity and *vice versa*. In order that an explosive wave may be produced, the mass of gas ignited must not be too small, and the cooling by radiation and conduction must not reduce the temperature below a particular point. The velocity of the chemical reaction must be such that the heat developed is sufficient to maintain the gaseous mixture at the required temperature. The propagation of a wave ceases when the theoretical temperature of the mixture falls below 2000 or 1700, according to the nature of the mixture, or when the volume of the products of combustion is less than one-fourth, or in some cases even one-third of the total volume of the final mixture. The limits below which an explosive wave is not formed are entirely different from the limits of combustion. They are much higher and vary according to the manner of ignition, and the nature of the initial impulse. As the limit is approached, the velocity of transmission falls considerably below its theoretical value. The establishment of a definite phase is effected only when the igniting sparks are somewhat powerful; with feeble sparks, the period of variable condition is much prolonged. The fulminates employed to register the progress of transmission appear to assist the gaseous column to assume a definite phase of detonation, as a result of the pressure which they develop. C. H. B.

**Influence of Mass on Chemical Action.** By J. MORRIS (*Annalen*, 213, 253—284).—In these experiments, solutions of potassium chromate and carbonate, or potassium sulphate and carbonate were mixed, and a solution of barium chloride run in. In each series of experiments, the amount of carbonate was variable, that of the other

salts being constant. From the results obtained in this way, the author draws the following conclusions:—

The course of the reaction is determined by the relative masses of the potassium salts, each yielding so much of its acid to the precipitate that the ratio to each other of the unaltered salts remaining in the filtrate is nearly constant.

The variation in the composition of the precipitate does not proceed by steps, but is continuous.

That in the simultaneous action of chromic and carbonic acids, the carbonic acid has a much greater energy at 100° than at ordinary temperatures; whilst this is much less apparent in the sulphuric carbonic series.

The quantity of liquid employed for solution has, within pretty wide limits, no great influence on the end-products.

A. J. G.

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## Inorganic Chemistry.

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**A new Catalytic Reaction.** By G. WATSON (*Chem. News*, **46**, 9).—Hydrogen dioxide added to an ammoniacal nickel sulphate solution is decomposed, but nickel peroxide is not formed, for if it were then it would, by acting on the ammonia, set free nitrogen; the same reaction occurs with nickel hydroxide suspended in water, but no effect is produced by adding the peroxide to an acidified solution of nickel sulphate.  
E. W. P.

**Reactions of Sulphuryl Chloride.** By P. KÖCHLIN and K. HEUMANN (*Ber.*, **15**, 1736—1738).—Sulphuryl chloride acts more energetically on red than on yellow phosphorus, forming sulphurous anhydride and phosphorous chloride. Heated with metallic arsenic, it yields a mixture of arsenious oxide and chloride. Antimony is converted into the trichloride by sulphuryl chloride, but metallic tin and sodium are not strongly attacked by it. Charcoal and sulphur do not act on sulphuryl chloride. By the action of sulphuryl chloride on sodium benzoate, a mixture of benzoic chloride and anhydride is produced.  
W. C. W.

**Non-existence of Pentathionic Acid.** By W. SPRING (*Annalen*, **213**, 329—363).—By the action of  $S_2Cl_2$  on potassium sulphite, tetrathionate and trithionate are obtained; and by its action on potassium thiosulphate, tetrathionate is formed, some sulphur separating. The formation of trithionate in the first case is due to a reaction between potassium sulphite and tetrathionate, yielding trithionate and thiosulphate.

The author made numerous experiments which fully confirm his previous statement that Wackenroder's solution, when prepared with excess of sulphurous anhydride, has the power of decolorising indigo; hydrogen disulphide acting on a solution of sulphurous acid, yields tetrathionic acid, sulphur, and a liquid which decolorises indigo;

liquids which decolorise indigo are also obtained by the action of sulphurous acid on sodium thiosulphate and of dilute sulphuric acid on potassium thiosulphate. Potassium hyposulphite,  $K_2SO_3$ , is rapidly destroyed by hydrogen sulphide; as Takamatsu and Smith added hydrogen sulphide until the smell of sulphurous anhydride was no longer perceptible, this reaction probably accounts for their failure to obtain the indigo decoloration. Hyposulphites do not combine directly with sulphur.

The main portion of the paper is devoted to a criticism of the results of Stingl and Morawski (Abstr., 1879, 1012), Kessler (Abstr., 1880, 298), and of Takamatsu and Smith (Trans., 1880, 592). The author contends that the substance called pentathionic acid is a solution of sulphur in tetrathionic acid, basing his arguments on the following grounds:—That tetrathionic acid readily dissolves sulphur; that sulphur is precipitated by the action of hydroxides and carbonates; that the excess of sulphur can be removed by agitation with metals or lead peroxide; and finally, that all the analyses as yet published (50 in number) for pentathionic acid, free, or as salts, show an indefinite composition, the ratio of hydrogen to sulphur varying from 2 : 3.505 to 2 : 5.23, the mean of the whole being 2 : 4.506, and only two analyses out of the 50 giving the ratio 2 : 5.

The author has repeated the experiments of Lewes (Trans., 1881, 68), but has only obtained salts containing an amount of sulphur intermediate between that required for tetrathionate and pentathionate; the salts had an acid reaction, and were either acid salts or contained free acid.

A. J. G.

**Preparation of Selenium.** See Zorgite, p. 1269.

**Phosphorescence and Oxidation of Phosphorus.** By I. CORNE (*J. Pharm. Chim.* [5], 6, 17—19).—Phosphorus placed under water was exposed in the dark for two months to an atmosphere of oxygen at a reduced pressure, and constant temperature. Although, before the exposure, a stick of phosphorus readily glowed in the oxygen, yet at the end of the time stated no glowing took place when a stick of phosphorus was plunged into the gas.

From this, the author concludes that the glowing of phosphorus is due first to the volatilisation of the phosphorus and the subsequent oxidation of the particles of the vapour. He reasons that during the above experiment the phosphorus had volatilised, and the vapour passed into the gas, which had become saturated, so that when a stick of phosphorus was introduced no further volatilisation could take place, no oxidation, and consequently no phosphorescence. The above is equally true for a mixture of oxygen and nitrogen in any proportions. The activity of the oxygen is brought about by the volatilisation of the phosphorus. During the volatilisation, the amount of which varies with the temperature and total pressure of the gas, electricity is generated by the volatilisation of the phosphorus, whereby some of the oxygen is converted into ozone, and this oxidises the vapour with emission of light and heat.

By increasing the pressure, the volatilisation is impeded, and at a certain limit is too slow to ozonise the oxygen, and hence the non-

phosphorescence in oxygen gas at high pressures. If, however, the temperature is increased, the rate of volatilisation is increased, until at last the phosphorus takes fire.

All gases which hinder or prevent the formation of ozone, lessen or destroy phosphorescence, whilst the vapours of volatile liquids, as ether and oil of turpentine, condense on the surface of the phosphorus, enclosing it in a layer of the liquid, where it is under the same condition as when immersed in a liquid, it can oxidise but not glow.

L. T. O'S.

**Molecular Weights of Phosphorus Iodides.** By L. TROOST (*Compt. rend.*, **95**, 293—295).—*Phosphorus Di-iodide*.—The vapour-density was determined in an atmosphere of nitrogen under low pressures, at about 270°. Under these conditions, the volatilisation of the iodide is somewhat rapid, whilst its decomposition is very slow. The colour of its vapour resembles that of nitrogen tetroxide at 20°. The numbers obtained were 18.0 and 20.2; the number calculated for  $P_2I_4$  is 19.7.

*Phosphorus Tri-iodide*.—The vapour-density was determined under the same conditions as the di-iodide. The numbers obtained were 14.32 and 14.61; the density calculated for  $PI_3$  is 14.29. C. H. B.

**Hypophosphoric Acid.** By I. CORNE (*J. Pharm. Chim.* [5], **6**, 123—124).—Hypophosphoric acid,  $P_2O_4 \cdot 2H_2O$ , is prepared as follows:—A glass flask of about 3 litres capacity, is closed with a cork in which is inserted a tube bent at right angles, and is about half filled with a solution of copper nitrate. To this is added 30—40 grams of phosphorus, and the flask is placed up to the neck in a water-bath, the temperature of which is gradually raised to 100°. A mixture of copper and copper phosphide is soon precipitated, which, when the temperature has reached 75°, rises to the surface of the liquid, and absorbs oxygen from the air, and a rapid and regular decomposition of the copper nitrate sets in. 12 grams of phosphorus are added from time to time (without removing the flask from the water-bath) until the colour of the solution has disappeared. The hypophosphoric acid is freed from the phosphoric acid and ammonia which is formed by saturating one-half the acid present with sodium carbonate. After a time sodium hypophosphate separates, and is purified by recrystallisation. By converting this into the lead salt and decomposing it with sulphuretted hydrogen, the free acid may be obtained. L. T. O'S.

**Volatilisation of Metals in a Vacuum.** By E. DEMARÇAY (*Compt. rend.*, **95**, 183—185).—In a Sprengel vacuum, cadmium volatilises slowly at a temperature of 160°, zinc at 184°, bismuth and antimony at 292°, tin and lead at 360°. The quantity of metal volatilised in 24 hours is sufficient to be weighed. At higher temperatures the rate of volatilisation increases; at 184°, for example, 0.1 gram of cadmium was volatilised in 20 hours. C. H. B.

**Solubility of Mixtures of Salts of the Alkalis and Alkaline Earths.** By H. PRECHT and B. WITTEGEN (*Ber.*, **13**, 1666—1672).—The following results were obtained, by treating a mixture of 210

grams  $\text{K}_2\text{SO}_4$  and 322 grams  $\text{NaCl}$  with an insufficient quantity of water for complete solution :—

$t^\circ$ .	100 parts of the saturated solution contain			100 parts of water dissolve		
	$\text{NaCl}$ .	$\text{K}_2\text{SO}_4$ .	$\text{KCl}$ .	$\text{NaCl}$ .	$\text{K}_2\text{SO}_4$ .	$\text{KCl}$ .
$10^\circ$ ....	23.1	5.6	2.2	33.43	8.10	3.18
20 ....	23.3	6.1	2.1	34.01	8.90	3.06
30 ....	23.5	6.5	2.0	34.56	9.56	2.95
50 ....	23.9	7.4	1.9	35.77	11.07	2.84
80 ....	23.5	8.0	3.3	36.04	12.26	5.06
100 ....	22.7	8.0	5.6	35.63	12.56	8.79

*Solubility and Degree of Decomposition of Magnesium Potassium Sulphate.*

$t^\circ$ .	100 parts of saturated solution contain		Ratio between the molecules of $\text{K}_2\text{SO}_4$ and $\text{MgSO}_4$ in the solution.	100 parts of water dissolve	
	$\text{K}_2\text{SO}_4$ .	$\text{MgSO}_4$ .		$\text{K}_2\text{SO}_4$ .	$\text{MgSO}_4$ .
$10^\circ$ ....	9.4	9.8	1 : 1.52	11.63	12.13
20 ....	10.9	10.8	1 : 1.43	13.92	13.79
30 ....	12.4	11.8	1 : 1.38	16.36	15.56
50 ....	14.7	14.8	1 : 1.46	20.85	20.99
70 ....	15.6	16.8	1 : 1.52	23.07	24.85

*Solubility of a Mixture of Potassium Magnesium Sulphate, and Sodium Chloride.*

	100 parts of the saturated solution contain			
	$\text{NaCl}$ .	$\text{K}_2\text{SO}_4$ .	$\text{MgSO}_4$ .	$\text{MgCl}_2$ .
$10^\circ$ .....	20.85	7.25	5.07	—
25 .....	20.67	8.50	6.05	—
35 .....	19.40	9.60	7.01	0.18
55 .....	18.65	12.89	8.64	0.45
65 .....	19.64	12.32	6.90	0.71
80 .....	15.50	14.30	4.70	4.20
100 .....	14.42	13.49	5.62	5.35

W. C. W.

**Removal of Iron from Zinc Sulphate.** By H. PRUNIER (*J. Pharm. Chim.* [5], 5, 608—609).—Iron which is present in zinc sulphate as monoxide may be completely separated by adding to 100 grams of the salt dissolved in 200 c.c. of water, just sufficient potassium permanganate to oxidise the iron (the quantity required is previously determined by titration), and a sufficient quantity of a decinormal ammonia solution to form a slight precipitate of zinc hydroxide (about 5 c.c. being sufficient). On boiling, the iron and manganese are completely precipitated; but should the supernatant liquid after the first boiling be coloured, a further quantity of ammonia is added, and the solution reboiled. When colourless, it is filtered, the filtrate concen-

trated, and allowed to crystallise. The usual method of oxidising the iron with nitric acid, and boiling with excess of zinc oxide, is objected to on the ground that the iron is not completely separated, and a basic sulphate of zinc is formed, which, together with zinc nitrate, is afterwards found in the sulphate. Chlorine is objected to, owing to the difficulty of its manipulation.

L. T. O'S.

**Action of Aluminium on Cupric Chloride.** By D. TOMMASI (*Chem. News*, **46**, 62).—Aluminium acts briskly on cupric chloride at the ordinary temperature, forming metallic copper, hydrogen, and aluminium oxychloride, whose composition varies with the temperature. If aluminium is allowed to act on this oxychloride, a compound having the formula  $\text{Al}_2\text{Cl}_6(\text{Al}_2\text{O}_3, 3\text{H}_2\text{O})_6, 12\text{H}_2\text{O}$  is produced. A solution of this compound is decomposed by a drop of sulphuric acid, a hydrate of aluminium being precipitated, which is but sparingly soluble in acid, and may be an isomeric modification of the trihydrate.

E. W. P.

**Action of Ammonia on Cupric Oxide.** By E. J. MAUMENÉ (*Compt. rend.*, **95**, 223—227).—Aqueous ammonia, free from ammonium salts, does not dissolve either cupric hydroxide or cupric oxide. The compound  $2\text{NH}_3, \text{CuO}$ , cuprammonium oxide, does not exist. In presence of ammonium sulphate, however, ammonia dissolves cupric hydroxide, and the deep-blue solution contains a basic salt,  $\text{SO}_3, \text{CuO}, 4\text{NH}_3$ . Copper carbonate dissolves in ammonia in presence of ammonium carbonate, forming the compound  $3\text{CO}_2, \text{CuO}, 4\text{NH}_3$ , and copper phosphate dissolves in ammonia in presence of ammonium phosphate, forming the compound  $\text{P}_2\text{O}_5, 2\text{CuO}, 8\text{NH}_3$ . All these compounds contain more than one equivalent of ammonia for each equivalent of copper.

C. H. B.

**A Basic Copper Sulphate.** By A. STEINMANN (*Ber.*, **15**, 1411—1412).—On heating a saturated solution of copper sulphate at 240—250°, a green crystalline salt is deposited, which is insoluble in water. This basic sulphate has the composition  $6\text{CuO}, 2\text{SO}_3 + 3\text{H}_2\text{O}$ .

W. C. W.

**Tin Nitrates.** By R. WEBER (*J. pr. Chem.* [2], **26**, 121—131).—During the process of mixing and pressing the damp constituents of gunpowder in the powder mills, it frequently happens that the materials take fire. It was observed at the German Government Powder Works at Spandau, that the solder (tin and lead) on the rollers had been attacked, or had entirely disappeared wherever it had come in contact with the damp materials, and, moreover, in the grooves thus formed a substance was found, which ignited when scraped out with a chisel. The author attributed this phenomenon to the presence of some nitro-compounds, and as lead nitrates are more stable than the corresponding tin salts, he concluded that it must be a nitrate of tin. The present knowledge of these compounds being very scanty, preliminary experiments were made. Moist potassium nitrate was found to have no action on tin; but nitric acid, strong or dilute, dissolves the metal without evolution of gas, provided the



temperature is kept low. Stannous nitrate is prepared by dissolving pure freshly-prepared stannous oxide in pure nitric acid, sp. gr. 1.20; the oxide is added as long as the liquid remains clear. When this solution is cooled to  $-20^{\circ}$ , the salt is deposited in thin transparent colourless leaflets, which melt very quickly after their removal from the cold liquid. The tin was determined in them by carefully adding strong nitric acid, and weighing as stannic oxide. The nitric acid was calculated from the quantity used, and the formula  $\text{SnN}_2\text{O}_6 \cdot 20\text{H}_2\text{O}$  was obtained. Besides this, another salt is formed, which is sparingly soluble, easily crystallisable, and can be obtained dry. It is a basic salt, probably  $\text{Sn}_2\text{N}_2\text{O}_7$ , is partially decomposed by water, and gradually oxidises and changes in the air. It can be heated to  $100^{\circ}$ ; at higher temperatures it is decomposed with explosion, the products being nitrous fumes and finely-divided stannic oxide. It also detonates strongly either by concussion or friction. It can be prepared: 1. If the above solution of stannous oxide in nitric acid is mixed with excess of the oxide at  $30-35^{\circ}$ , the basic salt is deposited as a greyish-white coherent crystalline mass, which is dried in the air and recrystallised from water; prepared in this way, however, it is generally mixed with oxide. 2. It can be obtained pure by adding sodium carbonate, with constant shaking, to the freshly-made nitric acid solution of stannous oxide; the precipitate of the basic salt thus obtained, forms snow-white granular aggregations of rectangular prisms. 3. When nitric acid (sp. gr. 1.20) is spread over sheets of tinfoil or of an alloy of tin and lead by means of a spray producer, the metallic surface becomes coated with this basic salt, which, when dry, burns with scintillation, or explodes when struck. 4. It is also formed when tin acts on metallic nitrates, *e.g.*, tinfoil and copper nitrate react; the tin speedily becomes covered with a mixture of precipitated copper and this basic salt; the final product, when dry, burns with scintillation, or, when suddenly heated or struck, explodes. 5. The conditions in the powder mill were reproduced thus:—A piece of tinfoil, placed in a dish with a damp mixture of nitre and sulphur, was covered by a piece of copper, so that only a thin film of the mixture was between the two metals; in a short time a considerable quantity of the basic tin nitrate had formed. The use of tin in rollers for gunpowder mills, therefore, must be avoided. D. A. L.

**Arsenates Neutral to Litmus.** By E. FILHOL and SENDERENS (*Compt. rend.*, 95, 343—344; see also *Abstr.*, 1881, 1101).—*Sesquisodium arsenate*,  $\text{As}_2\text{O}_5 \cdot 3\text{NaHO} + 3\text{H}_2\text{O}$ , or  $2\text{As}_2\text{O}_5 \cdot 3\text{Na}_2\text{O} \cdot 3\text{H}_2\text{O} + 6\text{H}_2\text{O}$ , obtained in the same way as the corresponding phosphate (this vol., 693), forms monoclinic crystals, which usually have the form of prisms truncated by faces of the octohedron. When heated, the crystals lose their water of crystallisation without melting. At a higher temperature, the salt fuses, and on cooling forms a vitreous mass which gradually becomes opaque. Above the temperature of fusion, the compound gradually decomposes and loses weight.

The authors were unable to obtain the corresponding potassium and ammonium salts. At a certain degree of concentration, the perfectly neutral solutions of these salts split up into acid crystals and an alkali-

line mother-liquor. Similar phenomena are observed with the corresponding phosphates.

Sodium potassium arsenate, however, crystallises in monoclinic octohedrons of the composition  $4\text{As}_2\text{O}_5, 3\text{Na}_2\text{O}, 3\text{K}_2\text{O}, 6\text{H}_2\text{O} + 18\text{H}_2\text{O}$ . The sodium-ammonium compound also crystallises in monoclinic octohedrons with 12 mols. water of crystallisation. This last salt is more stable than the corresponding phosphate, which only contains  $6\text{H}_2\text{O}$ ; the latter is easily decomposed by water, whilst the former is not appreciably affected. In fact the stability of these new phosphates and arsenates increases with the number of molecules of water of crystallisation with which they combine.

C. H. B.

**Preparation of Vanadium Trichloride.** By W. HALBERSTADT (*Ber.*, 15, 1619—1620).—A simple method of preparing vanadium trichloride is to warm vanadium trisulphide in a current of chlorine. The dark-brown liquid which distils over is a mixture of vanadium trichloride and sulphur chloride. To remove the chloride of sulphur, the mixture is redistilled, and the red residue is heated at  $150^\circ$  in a stream of carbonic anhydride.

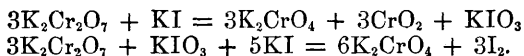
When an aqueous solution of vanadium trichloride is boiled with sodium thiosulphate, its colour changes from brown to blue and green. If the thiosulphate is present in large quantities, a dark precipitate, consisting of sulphide and oxide, is thrown down. When an electric current is passed through an aqueous solution of vanadium trichloride acidified with hydrochloric acid, a red soluble substance is formed at the positive pole.

W. C. W.

**Alkaline Reaction of Potassium Chromate.** By M. RICHTER (*Zeitsch. Anal. Chem.*, 21, 204).—The alkaline reaction of yellow potassium chromate may be due to three causes; it may be ascribed to impurities derived from the methods of preparation, to the chemical nature of the salt, or to the oxidising power of chromic acid. Potassium chromate six times recrystallised from water and precipitated by alcohol did not lose its alkaline reaction. Its solution gave with turmeric a strong brown, with red litmus-paper a bluish-green coloration, but was without action on phenolphthaleïn. The author concludes that the chromic acid oxidises the colouring matters of litmus and turmeric, free alkali being formed, but is without chemical action on phenolphthaleïn.

O. H.

**Action of Potassium Dichromate on Potassium Iodide.** By M. RICHTER (*Zeitsch. Anal. Chem.*, 21, 368—374).—E. Donath has recently stated (*Zeitsch. Anal. Chem.*, 18, 78, and 19, 19) that whilst chromic acid readily separates free iodine from iodides, potassium dichromate is without action, and he proposed the difference in the behaviour towards potassium iodide as a test for free chromic acid in potassium dichromate. Richter contradicts Donath's statement, and shows that chemically pure dichromate is readily, and after some length of time completely, decomposed by potassium iodide, the reaction taking place in two stages, expressed by the following formulæ:—



In reference to a statement made by F. Mohr, that potassium chromate when heated with ammonium chloride liberates ammonia, and should therefore be considered as a basic salt, the dichromate being the really neutral salt, the author believes that the slight evolution of ammonia which actually takes place is simply due to the dissociation of the ammonium chromate which is formed, crystals of this salt giving off ammonia even at ordinary temperatures. O. H.

**Uranium.** By C. ZIMMERMANN (*Annalen*, 213, 285—329).—Most of the results contained in this paper have already appeared (*Abstr.*, 1881, 686, 759). Uranyl salts in sulphuric acid solution are reduced by zinc to uranous salts, the liquid assuming a green colour. In hydrochloric acid solution, the reduction proceeds further, uranium subchloride,  $\text{Ur}_2\text{Cl}_6$ , being formed, the solution turning first green and finally red. Drawings are given of the absorption-spectra, corresponding to the various degrees of reduction. A. J. G.

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## Mineralogical Chemistry.

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**Development of a Crystal of one Substance in the Solution of another.** By H. KOPP (*Ber.*, 15, 1653—1655).—With reference to Arzruni's article on isomorphism (*N. Handwörterb. Chem.*, 3, 840), the author maintains that two bodies are isomorphous when a crystal of one substance continues to grow in a solution of the other. Numerous attempts to repeat Wackernagel's experiments (*Kastner's Archiv.*, 5, 293) of growing alum on a crystal of boracite, or lead nitrate on a crystal of alum, yielded negative results. W. C. W.

**Origin and Formation of the Diamond in Nature.** By A. B. GRIFFITHS (*Chem. News*, 46, 105).—The author considers that the diamond has been formed by the action of highly heated water or water-gas, aided by great pressure, on the carbonaceous matter of fossils in the sedimentary rocks, followed by cooling, and consequent deposition of the carbon in the crystalline condition. E. W. P.

**Cause of the Blue Colour of Sapphire, the Green of Emerald, and the Purple of Amethyst.** By W. A. ROSS (*Chem. News*, 46, 33).

**Zorgite, a Selenium Mineral from the Argentine Republic.** By BILLAUDOT (*J. Pharm. Chim.* [5], 5, 595—597).—From 139.5 kilos. of zorgite of the following composition—

Se.	Cu.	Pb.	Fe.	Hg.	Sand and SiO <sub>2</sub> .
30.80	15.00	41.00	6.00	1.66	4.60

the author has obtained 37 kilos. of selenium by treating it with aqua regia ( $5\text{HCl} : 1\text{HNO}_3$ ,  $36^\circ \text{B.}$ ), evaporating at a gentle heat, filtering from lead chloride, and passing sulphurous anhydride through the solution. The precipitated selenium was washed with water, to free it from copper chloride, boiled with hydrochloric acid to free it from lead chloride, and finally washed with water, dried, and melted. Great difficulty was experienced in obtaining bars of vitreous selenium. When it was cast in cast-iron moulds, the cooling was so slow that the graphitic modification was obtained. By casting in copper moulds with thin walls, plates of vitreous selenium 0.5 cm. thick were obtained, but the best results were gained by placing the mould in water, and pouring in the melted selenium when it had cooled nearly to the solidifying point; it then immediately solidified in the vitreous modification. A bar 3 cm. thick, and weighing 12.6 kilos., was thus obtained.

L. T. O'S.

**Artificial Production of Calcite and Witherite.** By MIRON and BRUNEAU (*Compt. rend.*, **95**, 182—183).—If river water is employed to work an aspirator which is aspirating air charged with ammonia gas, the ammonia neutralises the free carbonic acid in the water, and the calcium carbonate previously held in solution is deposited in the exit tube in the form of crystals of calcite. Crystals of witherite are obtained by using in a similar manner a solution of barium carbonate in distilled water charged with carbonic acid.

C. H. B.

**Presence of Manganese on the Surface of Rocks.** By BOUSSINGAULT (*Compt. rend.*, **95**, 318—324).—According to different travellers, the granite rocks on the banks of the Orinoco and its tributaries, and similar rocks in the valley of the Nile, on the borders of the Red Sea, and on the banks of the Congo, are covered with a thin shining greyish-black metallic-looking layer, which contains a large proportion of oxides of manganese and iron. This layer is found only on the banks of rivers subject to periodic risings, having a mean temperature between  $24^\circ$  and  $28^\circ$ , and flowing over granite, gneiss, and hornblende rocks. At the cascades at the source of the Coconuco, in the Andes, the author has observed a similar layer, coating a white translucent calcareous mass which cements together the blocks of trachyte over which the cascade falls. Analyses of the water and of the calcareous deposit gave the following results:—

	$\text{Na}_2\text{SO}_4$ .	$\text{NaCl}$ .	$\text{NaHCO}_3$ .	$\text{CaCO}_3$ .	$\text{MnCO}_3$ .
(1.) Water ..	3.89	2.75	0.69	0.10	
(2.) Deposit.	1.0		—	74.2	21.0
	$\text{MgCO}_3$ .	$\text{SiO}_2$ .			
(1.) Water. . .	—	traces =	7.43 grams per litre.		
(2.) Deposit ..	4.0	— =	100.2        „		

The deposit is evidently a dolomite, in which magnesium is replaced by manganese, and the black outer layer is the result of the oxidation of the manganese carbonate by the action of the air.

The presence of manganese in mineral waters, especially in those

from hot springs, has been proved by several observers. The black superficial layer on the rocks on the banks of the rivers previously mentioned is in all probability due to the presence in the water of manganese carbonate, which is first deposited on the rocks, and subsequently oxidised.

C. H. B.

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## Organic Chemistry.

**Normal Paraffins.** Part I. By F. KRAFFT (*Ber.*, **15**, 1687—1711).—The higher paraffins can be prepared from fatty acids by two methods.

*a.* A mixture of from 2—4 grams of the acid, 3—4 grams of hydriodic acid (sp. gr. 1.7), and 0.3—0.4 gram of amorphous phosphorus is heated at 210—240° in sealed tubes for 3—5 hours. The tubes must be opened before any appreciable quantity of iodine is set free, fresh phosphorus is then added, and the tubes are resealed and again heated for 3—5 hours. The tubes must again be opened for the purpose of adding phosphorus and a small quantity of water. They are then heated for the last time. Water is added to the crude product. The hydrocarbon which floats on the surface of the mixture is syphoned off and purified by distillation under reduced pressure and treatment with potash.

*b.* The hydrocarbons can also be prepared from the ketones obtained by distilling the barium salt of a fatty acid with barium acetate. The ketone is heated with excess of phosphorus pentachloride in an oil-bath at 200°, and the operation is interrupted when most of the excess of phosphorus chloride has distilled over, and before the mixture begins to blacken. The hydrocarbon is easily obtained from the crude product by heating it with hydriodic acid and phosphorus in sealed tubes.

*Normal nonane*,  $C_9H_{20}$ , is prepared from nonoic acid, which is best obtained by fusing undecylenic acid with potash (*Ber.*, **10**, 2035; **11**, 1413). The hydrocarbon melts at  $-51^\circ$ , and boils at  $39.5^\circ$  under 11 mm. pressure, at  $86^\circ$  under 100 mm., and at  $149.5^\circ$  under 760 mm. pressure. Its sp. gr. compared with water at  $4^\circ$ , is 0.733 at  $0^\circ$ , and 0.7217 at  $15^\circ$ .

*Normal decane*,  $C_{10}H_{22}$ , is prepared from capric acid or from the ketone  $C_{10}H_{20}O$ , formed by distilling a mixture of barium nonoate and acetate. The ketone melts at  $3.5^\circ$ , boils at  $211^\circ$ , and has the sp. gr. 0.8379 at its melting point. The hydrocarbon melts at  $-32^\circ$ , and boils at  $173^\circ$ ; its sp. gr. at  $0^\circ$  is 0.7456.

*Undecane* obtained from undecoic acid, or from the ketone  $C_{11}H_{22}O$ , contained in oil of rue, melts at  $-26.5^\circ$ , and boils at  $74^\circ$  under 11 mm. pressure, at  $127^\circ$  under 100 mm., and at  $194.5^\circ$  under 760 mm. pressure. *Dodecane*, obtained by the reduction of lauric acid, melts at  $-12^\circ$ , boils at  $214.5^\circ$ , and has the sp. gr. 0.7655 at  $0^\circ$ , and 0.7511 at  $20^\circ$ . *Tridecane*, prepared from the ketone  $C_{13}H_{26}O$  (m. p.  $28^\circ$ ), and also from tridecoic acid, melts at  $6.2^\circ$ , boils at  $234^\circ$ , and has the sp. gr. 0.7713 at  $0^\circ$ . The higher hydrocarbons exhibit the following

physical properties:—*Tetradecane*, from myristic acid, m. p.  $4\cdot5^{\circ}$ ; b. p.  $252\cdot5^{\circ}$ ; sp. gr. at  $4\cdot5^{\circ} = 0\cdot7753$ ; at  $20^{\circ} = 0\cdot7645$ . *Pentadecane*, from pentadecic acid, or from the ketone  $C_{15}H_{30}O$  (m. p.  $39^{\circ}$ , obtained from barium myristate), m. p.  $10^{\circ}$ ; b. p.  $270\cdot5^{\circ}$ ; sp. gr.  $0\cdot7759$  at  $10^{\circ}$ . *Hexadecane*, m. p.  $18^{\circ}$ ; b. p.  $287\cdot5^{\circ}$ , under 760 mm. pressure; sp. gr.  $0\cdot7754$  at  $18^{\circ}$ . *Heptadecane* (from margaric acid, or from the ketone  $C_{17}H_{34}O$ , obtained from barium palmitate), crystallises in large hexagonal plates, m. p.  $22\cdot5^{\circ}$ ; sp. gr.  $0\cdot7767$  at  $22\cdot5^{\circ}$ ; it boils at  $303^{\circ}$ . *Octadecane* from stearic acid, m. p.  $28^{\circ}$ ; b. p.  $317^{\circ}$ ; sp. gr. at  $28^{\circ} = 0\cdot7768$ . *Nonadecane*, prepared from the ketone  $C_{19}H_{38}O$ , melts at  $32^{\circ}$ ; boils at  $330^{\circ}$ ; and has the sp. gr.  $0\cdot7774$  at  $32^{\circ}$ .

The ketone  $C_{19}H_{38}O$ , obtained by distilling a mixture of barium stearate and acetate, yields margaric acid,  $C_{17}H_{34}O_2$ , on oxidation. By repeating these reactions it is possible to descend through the series of fatty acids from stearic to nonoic acid. The following table shows the boiling and melting points of these acids and ketones. The boiling points were determined under 100 mm. pressure, and with the stem of the thermometer immersed in the vapour up to the 150th degree.

Acid.	M. p.	B. p.	Ketone.	M. p.	B. p.
$C_{18}H_{36}O_2$ ..	$69\cdot2^{\circ}$	$287^{\circ}$	$C_{19}H_{38}O$ ..	$55\cdot5^{\circ}$	$262\cdot5$
$C_{17}H_{34}O_2$ ..	$59\cdot8$	$277$	$C_{18}H_{36}O$ ..	$51\cdot5$	$251\cdot5$
$C_{16}H_{32}O_2$ ..	$62$	$268\cdot5$	$C_{17}H_{34}O$ ..	$48$	$242$
$C_{15}H_{30}O_2$ ..	$51$	$257$	$C_{16}H_{32}O$ ..	$43\cdot5$	$230\cdot5$
$C_{14}H_{28}O_2$ ..	$53\cdot8$	$248$	$C_{15}H_{30}O$ ..	$39$	$219$
$C_{13}H_{26}O_2$ ..	$40\cdot5$	$236$	$C_{14}H_{28}O$ ..	$33\cdot5$	$205\cdot5$
$C_{12}H_{24}O_2$ ..	$43\cdot6$	$225$	$C_{13}H_{26}O$ ..	$28$	$191\cdot5$
$C_{11}H_{22}O_2$ ..	$28$	$212\cdot5$	$C_{12}H_{24}O$ ..	$21$	$177\cdot5$
$C_{10}H_{20}O_2$ ..	$31\cdot4$	$200$	$C_{11}H_{22}O$ ..	$13$	$161$
$C_9H_{18}O_2$ ..	$12\cdot5$	$186$	$C_{10}H_{20}O$ ..	$3\cdot5$	$142$

W. C. W.

**Normal Paraffins. A Law of Volumes for the Liquid State.** Part II. By F. KRAFFT (*Ber.*, 15, 1711—1727).—Paraffins containing 23, 27, 31, and 35 atoms of carbon respectively were prepared from the ketones, laurone, myristone, palmitone, and stearone. Ketones containing 20, 22, and 24 atoms were prepared by distilling barium heptate with barium myristate, palmitate, and stearate respectively. The properties of the hydrocarbons and of some of the ketones are seen from the following tables:—

Ketones.	M. p.	Sp. gr. at m. p.	Mol. vol.
$C_{13}H_{26}O$ .....	$28^{\circ}$	$0\cdot8229$	$246\cdot6$
$C_{15}H_{30}O$ .....	$39$	$0\cdot8182$	$276\cdot2$
$C_{17}H_{34}O$ ..	$48$	$0\cdot8140$	$312$
$C_{19}H_{38}O$ .....	$55\cdot5$	$0\cdot8108$	$347\cdot8$
$C_{23}H_{46}O$ .....	$69$	$0\cdot8036$	$420\cdot6$
$C_{27}H_{54}O$ .....	$72\cdot3$	$0\cdot8013$	$491\cdot7$
$C_{31}H_{62}O$ .....	$82\cdot8$	$0\cdot7997$	$562\cdot7$
$C_{35}H_{70}O$ .....	$88\cdot4$	$0\cdot7979$	$634\cdot1$

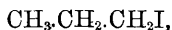


Hydrocarbons.	M. p.	Sp. gr. at m. p.	Mol. vol.	B. p. under 15 mm. pressure.	Difference between m. p. and b. p.
C <sub>11</sub> H <sub>24</sub> .....	- 26·5°	0·7745	201·4	81°	107·5°
C <sub>12</sub> H <sub>26</sub> .....	- 12	0·7731	219·9	98	110
C <sub>13</sub> H <sub>28</sub> .....	- 6·2	0·7755	237·3	114	120·2
C <sub>14</sub> H <sub>30</sub> .....	+ 4·5	0·7753	255·4	129·5	125
C <sub>15</sub> H <sub>32</sub> .....	+ 10	0·7758	273·2	144	134
C <sub>16</sub> H <sub>34</sub> .....	+ 18	0·7754	291·4	157·5	139·5
C <sub>17</sub> H <sub>36</sub> .....	+ 22·5	0·7767	309·0	170	147·5
C <sub>18</sub> H <sub>38</sub> .....	+ 28	0·7768	326·9	181·5	153·5
C <sub>19</sub> H <sub>40</sub> .....	+ 32	0·7774	344·7	193	161
C <sub>20</sub> H <sub>42</sub> .....	36·7	0·7779	362·5	205	168·3
C <sub>21</sub> H <sub>44</sub> .....	40·4	0·7783	380·3	215	174·6
C <sub>22</sub> H <sub>46</sub> .....	44·4	0·7782	398·3	224·5	180·1
C <sub>23</sub> H <sub>48</sub> .....	47·7	0·7785	416·2	234	186·3
C <sub>24</sub> H <sub>50</sub> .....	51·1	0·7786	434·1	243	191·9
C <sub>27</sub> H <sub>56</sub> .....	59·5	0·7796	487·4	270	210·5
C <sub>31</sub> H <sub>64</sub> .....	68·1	0·7808	558·4	302	233·9
C <sub>35</sub> H <sub>72</sub> .....	74·7	0·7816	629·4	331	256·3

From the above data, the author draws the conclusion that equal volumes of different liquids have the same weight, when the compounds possess similar percentage composition, and exhibit the same relation between their molecular weights and the total amount of heat contained in them.

W. C. W.

**Trimethylene.** By A. FREUND (*Monatsh. Chem.*, **3**, 625—635).—In a former paper (p. 154 of this volume) the author announced the isolation of this hydrocarbon by the action of sodium on the bromide of trimethylene or normal propylene, and the formation of this latter compound, CH<sub>2</sub>Br.CH<sub>2</sub>.CH<sub>2</sub>Br, and of normal propyl iodide,



by its direct union with bromine and with hydrogen iodide respectively, the combination in both cases taking place much more readily than with ordinary propylene. In the present communication he describes the apparatus used in effecting these combinations, and the mode of working, and finally discusses the constitution of the hydrocarbon, pointing out that on the supposition of its containing bivalent carbon, it might be represented by the formula CH<sub>3</sub>.C.CH<sub>3</sub> or by CH<sub>3</sub>.CH<sub>2</sub>.CH, but that its reactions with bromine, potassium hydroxide, &c., show that its true formula is that of trimethylene, CH<sub>2</sub>.CH<sub>2</sub>.CH<sub>2</sub>.

[ ]

H. W.

**Nitrils of the Higher Members of the Acetic Acid Series.** By F. KRAFFT and B. STAUFFER (*Ber.*, **15**, 1728—1731).—*Lauramide*, C<sub>12</sub>H<sub>25</sub>NO (m. p. 102°), is best prepared by gently warming a mixture of phosphorus pentachloride and lauric acid, and pouring the resulting oily liquid when cold into an excess of (well-cooled) strong

ammonia. The precipitated amide is obtained in a state of purity by recrystallisation from alcohol.

When a mixture of the amide and phosphorus pentoxide is heated in a retort under a pressure of 11 mm., *lauronitril*,  $C_{12}H_{23}N$ , distils over. This substance melts at  $4^\circ$ , boils at  $198^\circ$  under 100 mm. pressure. Its sp. gr. at  $4^\circ = 0.8350$ . *Myristamide*,  $C_{14}H_{29}NO$ , melts at  $104^\circ$ . The nitril melts at  $19^\circ$ , boils at  $226.5^\circ$  under 100 mm. pressure. Its sp. gr. at  $19^\circ$  is 0.8281. *Palmitamide*,  $C_{16}H_{33}NO$ , melts at  $106^\circ$ . *Palmitonitril* crystallises in six-sided plates (m. p.  $31^\circ$ ). It boils at  $251.5^\circ$  under 100 mm. pressure, and its sp. gr. at the melting point is 0.8224. *Stearamide*,  $C_{18}H_{37}NO$ , melts at  $109^\circ$ . The nitril,  $C_{18}H_{35}N$ , melts at  $41^\circ$ , and boils at  $274.5^\circ$  under 100 mm. pressure. Its sp. gr. at  $41^\circ$  is 0.8178.

W. C. W.

**Conversion of Perthiocyanic Acid into Potassium Thiocyanate.** By A. STEINER (*Ber.*, 15, 1603—1604).—The perthiocyanic acid which is obtained as a bye-product in the preparation of carbonyl sulphide by Than's method, can be converted into potassium thiocyanate by dissolving the acid in a dilute solution of potassium cyanide, and evaporating the liquid on a water-bath. This method yields quantitative results.

W. C. W.

**Solubility of Anhydrous Copper Sulphate in Methyl Alcohol.** By A. KLEPL (*J. pr. Chem.* [2], 25, 526—527).—When chemically pure and dry methyl alcohol is shaken with dry copper sulphate, it assumes after some time a bluish-green colour, owing to the copper sulphate dissolved, whilst the undissolved salt remains white. If now about one-tenth of its volume of water and a little more anhydrous copper sulphate are added to this solution, the water and the dissolved copper sulphate are precipitated, the alcohol becomes colourless, and contains scarcely a trace of copper. Hence aqueous methyl alcohol will give up the water to anhydrous copper sulphate without dissolving the salt. On the other hand, if the salt is dissolved, then the methyl alcohol is free from or contains extremely little water. Absolute methyl alcohol therefore differs from ethyl alcohol in being a solvent for anhydrous copper sulphate.

D. A. L.

**Preparation of Pure Starch-sugar.** By F. SOXHLET (*Dingl. polyt. J.*, 245, 121—125).—For the preparation of pure anhydrous dextroglucose,  $C_6H_{12}O_6$ , the author evaporates a solution of starch-sugar in a vacuum, until a sample on cooling can only just be kneaded into a dough. The syrupy mass thus obtained is mixed in closed vessels with boiling-hot methyl alcohol, the quantity required depending on the purity of the starch-sugar and the quality of the product. For ordinary (20 to 30 per cent.) starch-sugar, 100 parts of syrup require 70—80 parts alcohol. The crystallisation is facilitated by adding anhydrous crystallised starch-sugar. The granular mass is separated from the liquid by machining and pressing. Granular porous starch-sugar is obtained in the form of solid lumps of well-formed shining crystals, resembling refined loaf-sugar, by concentrating a perfectly clear, colourless solution of starch-sugar in a vacuum. The

syrup should remain quite clear. 100 parts of the latter are mixed at 70° with 10—25 parts boiling hot pure methyl alcohol. The mixture is then poured into conical moulds, cooled to 30—35°, and kept at this temperature for 2 or 3 days, when the liquid is drawn off. If dense and solid sugar is required, the porous mass, after the removal of the liquid, is saturated once or twice with a mixture of 100 parts concentrated syrup and 80—100 parts alcohol at the ordinary temperature, until the necessary density has been reached. The liquid is then drawn off, the mass treated with alcohol, pressed, and the alcohol removed by distillation in a vacuum at a temperature increasing slowly from 30° to 60°. The sugar is kept at this temperature for several hours. The starch-sugar hitherto prepared contains, besides water, 20—30 per cent. uncrystallisable and unfermentable substances of gum-like consistency. To produce pure starch-sugar of crystalline structure, Soxhlet proposes to remove the impurities by means of ethyl and methyl alcohol, and to crystallise the purified and sufficiently concentrated product at above 30°. Solid translucent starch-sugar (ordinary hydrated glucose) of distinctly crystalline structure, is obtained by cooling the syrup from starch-sugar at above 30°. While the solutions of starch-sugar solidify at the ordinary temperature in layers of opaque, warty, microscopical tabular crystals, the mass obtained at a temperature above 30°, from more concentrated solutions, forms transparent prismatic crystals distinctly visible to the naked eye.

D. B.

**Preparation of Grape-sugar by Neubauer's Modification of Schwarz's Method.** By W. MÜLLER (*J. pr. Chem.* [2], 26, 78—87).—In reply to Soxhlet (*ibid.*, 21, 227—317), the author states that pure grape-sugar can be prepared by the above process; and that Knapp's solution can be used for the titration of grape-sugar. These statements are proved experimentally. From a series of experiments he infers that the most efficient solution for the inversion of the raw sugar is 600 of alcohol to 40 of fuming hydrochloric acid, the temperature should be about 15°, and the duration of the experiment from 3 to 4 weeks. When the solvent contains less hydrochloric acid, or when the temperature is too low, only a comparatively small quantity of the raw sugar is dissolved, and therefore the grape-sugar which is formed takes a very long time to deposit; on the other hand, with stronger solutions of hydrochloric acid, or with higher temperatures, the solutions are always discoloured. The author has prepared pure grape-sugar in the following manner:—As much raw sugar as will dissolve is added to the solution of 40 c.c. hydrochloric acid in 600 c.c. of alcohol, at the ordinary temperature, the solution is repeatedly shaken, and after 3 or 4 weeks is filtered and left to crystallise. Crystallisation is complete in about 6 weeks, the crystals are separated from the liquid by filtration on a vacuum filter, well washed by grinding with small quantities of 90 per cent. alcohol, and left in it for a day and again collected; this operation is repeated until the washings have no acid reaction; this washing is of the utmost importance. The sugar thus prepared is quite pure, and after drying over chloride of calcium, melts at 146°, and gives a clear colourless solution; it is not blackened by concentrated sulphuric acid.

Knapp's solution can be successfully employed for the titration of grape-sugar, provided the solution is diluted, and the sugar added gradually. In the appended tables are the results of the titration of the same sugar by Fehling and Knapp solutions.

	Fehling.	Knapp.
3 per cent. aqueous solution grape-sugar ..	3.03	3.01
2    "                   "                   " ..	2.03	2.0
1    "                   "                   " ..	1.01	1.01

Solutions of grape-sugar in urine—

With 3 per cent. of sugar .....	3.12	2.94
2    "                   " .....	2.16	2.19
1    "                   " .....	1.13	1.19

D. A. L.

**Preparation of Grape-sugar and its Titration with Knapp's Solution.** By J. G. OTTO (*J. pr. Chem.* [2], 26, 87—103).—This paper, like that of W. Müller (preceding Abstract), is in answer to Soxhlet (Abstr., 1880, 758). The author finds the process adopted by Müller (*loc. cit.*) the most economical and also the most efficient method for the preparation of glucose, and obtains the largest yields under these conditions. Dissolve 230 grams raw sugar in 600 c.c. 80 per cent. alcohol + 20 c.c. hydrochloric acid, keeping the temperature at 25°; subsequent treatment is the same as described in Müller's paper. The author has likewise improved the process used by Soxhlet, inasmuch as he has shortened the time occupied in crystallising the glucose from alcohol, thus: a saturated solution of grape-sugar in alcohol is made by boiling them together in a flask with reflux condenser, and filtered through a hot-water filter into a flask cooled by a stream of cold water, the crystallisation being complete after standing 24 hours in a cold place. The crystals are then washed with alcohol and dried over calcium chloride or sulphuric acid. The process is superior to the other as regards quickness, but is less economical. Some grape-sugar crystallised from methyl alcohol was compared with the above products, and all three were found to be alike. With regard to the use of Knapp's solution, the author has found that for solutions containing 1 to 0.5 per cent. sugar, it ought to be diluted with 4 vols. of water, for those of 0.5 to 0.1 per cent. with 3 vols. of water, whilst for sugar solutions containing less than 1 per cent., 2 vols. water should be added; besides this, the sugar must be run in by degrees. The author proceeded as follows:—About the required quantity of Knapp's solution is diluted (as required) with water, the sugar solution is run in 2 c.c. at a time, the mixture being boiled for half a minute between each addition, the mercury is allowed to settle and the clear solution tested by Pillitz's reaction; towards the end of the reaction, the sugar is run in by smaller quantities (1—0.5—0.2 c.c.) at a time. As soon as the test on the filter-paper becomes doubtful, the filtrate is tested with acetic acid and hydrogen sulphide, until there is no more mercury in solution. The author has obtained these results:—

With a Knapp's solution + 3 vols. water: in a 1 per cent. sugar

solution he found 0.992 per cent.; in a 0.5 per cent. solution, 0.498 per cent.; in a 0.25 solution, 0.249; in a 0.10 solution, 0.1; in a 0.05 solution, 0.049. With Knapp's solution + 4 vols. water, in the case of the 1 and 0.5 per cent. solution, the result was the same, but in the 0.25 solution it was too high. With a Knapp's solution + 2 vols. water, the result in the 0.1 per cent. solution was like the above, whilst in the 0.5 solution it was more exact. In each case, about 0.5 c.c. of sugar solution was added after Pillitz's reaction ceased to act, before all the mercury, rendered evident by the hydrogen sulphide and acetic acid, had disappeared. It is always advisable to dilute the sugar solution to about 1 per cent. or less before titrating.

D. A. L.

**Influence of Invertin on the Fermentation of Cane-sugar.** (*Dingl. polyt. J.*, **245**, 47).—Cane-sugar is not directly fermentable, but is resolved into dextrose and lævulose by inversion with dilute acids or by means of the invertin of yeast. According to Berthelot and Bechamp, the conversion of invertin takes place outside the cell, and in a very short time; the ferment being diffused in the outer liquid, and effecting the conversion of sugar indefinitely and independently of the fermenting process. Hence, in practice, substances containing cane-sugar are fermented without inversion with acid, the fermentation of the inverted sugar being supposed to take place less rapidly than the conversion of cane-sugar by the invertin contained in yeast. According to Bauer, 40 grams of cane-sugar were inverted with hydrochloric acid, the solution was neutralised with potash-ley, and treated with 5 grams of beer-yeast and 1 c.c. of a saturated solution of tartaric acid. The mixture was then made up with water to 400 c.c. In another experiment 40 grams of cane-sugar were treated with 0.86 gram potassium chloride, without inversion, and fermented in a similar manner at 30°. The quantities of carbonic anhydride evolved were—

	In 19 hours.	42 hours.	68 hours.
	g.	g.	g.
Inverted .....	1.0	4.0	7.8
Cane-sugar .....	0.1	2.1	5.1

The fermentation of the inverted sample was in the commencement considerably in advance of that of the uninverted sample. The increase in the rapidity of the fermentation in the case of cane-sugar, is due to the fact that by the simultaneous action of acid and invertin, constantly increasing quantities of grape-sugar are produced.

D. B.

**Formaldehyde or Oxymethylene.** By B. TOLLENS (*Ber.*, **15**, 1629—1634).—After referring to the researches of Baeyer (*Ber.*, **3**, 66), Wurtz (*Ber.*, **5**, 534), and Reinke (*Ber.*, **14**, 1249, this vol., 243), on the relation between formaldehyde and the glucoses, the author describes a modification of Hofmann's apparatus (*Ber.*, **1**, 152; **2**, 156; *Ann.*, **145**, 357) for preparing formaldehyde from methyl alcohol. The water-bath in which the flask containing the methyl alcohol is heated, is provided with Reichardt's thermoregulator, which prevents

the temperature from varying more than one or two degrees. Instead of a platinum tube, a tube of Bohemian glass is used, in which coils of platinum foil and wire are placed. Two wash-bottles containing water are attached to the receiver connected with the condenser. The different parts of the apparatus must be connected together without the use of corks or caoutchouc. When the tube containing the platinum has been heated for a few minutes at the desired temperature, the apparatus can be left to itself for hours. 100 grams of pure methyl alcohol yield from 60 to 80 grams of crude aldehyde, containing from 1.44 to 3.55 per cent. of formaldehyde, and from 0.1 to 0.8 per cent. of trimethylene oxide. The yield depends on the temperature of the platinum coils. The gases which escape from the apparatus do not support combustion. They contain from 6.67 to 8.33 per cent. of carbonic anhydride, and only 4.33—4.56 per cent. of oxygen.

The greater part of the methyl alcohol in the distillate can be removed by distillation. On evaporating the residue over sulphuric acid, trimethylene oxide remains in a crystalline form: the vapour-density of this substance, compared with hydrogen, was found to be 15.1. Trimethylene oxide dissolves in alkaline liquids. It also dissolves when heated at 100° in sealed tubes containing water; and the aqueous solution, when evaporated, deposits needle-shaped crystals.

The yellow precipitate which is deposited when crude formaldehyde or trimethylene oxide is treated with hot alkaline solutions, reduces Fehling's solution, but has no action on polarised light. When the apparatus used for preparing formaldehyde was fitted up with caoutchouc tubing and corks, the formation of a crystalline compound was observed, when the aldehyde prepared in this apparatus was mixed with 2 per cent. of crystalline baryta and evaporated over sulphuric acid. When caoutchouc was not used in fitting up the apparatus, this compound could no longer be obtained.

W. C. W.

**New Derivatives of Isobutaldehyde.** By W. FOSSEK (*Monatsh. Chem.*, **3**, 622—624).—In a former paper (this vol., p. 160), the author examined the products formed by the action of sodium acetate on isobutaldehyde, whereby he obtained chiefly two bodies,  $C_8H_{14}O$ , and  $C_8H_{16}O_2$ ; and in the present communication (a preliminary notice) he describes the action of other dehydrating agents, namely, zinc chloride, stannic chloride and sulphuric acid, on the same aldehyde. These substances, when employed in small quantities, exert on isobutaldehyde merely a polymerising action; but when applied in larger quantities, they give rise, under certain conditions, to the formation of liquid and crystallised bodies, which, though they are all probably formed in the same way, namely by separation of water, are nevertheless different in physical and chemical properties, both from one another and from the products obtained by the action of sodium acetate.

By treating isobutaldehyde with phosphorus trichloride, which is employed as a dehydrant in the conversion of ethers of the hydroxy-acids into those of the oleic acids, no condensation-products were obtained, but an oily and a crystallised derivative of the aldehyde were formed, containing phosphorus and chlorine. Small quantities

of phosphorus trichloride likewise gave rise to the conversion of the aldehyde into the trimolecular polymeric modification.

Dilute potash-ley, besides forming condensation-products by abstraction of water, likewise exerts an oxidising and a reducing action, thereby producing isobutyric acid and isobutyl alcohol, together with acids and alcohols containing twice the number of carbon-atoms, amongst which the author distinguished a crystalline acid,  $C_8H_{16}O_3$ , not volatilising with aqueous vapour, and melting at  $75-80^\circ$ ; and from the oily products of the reaction he was able to separate two neutral crystalline bodies, both having the empirical formula  $C_8H_{18}O_2$ , but differing from one another in their properties. One of these bodies forms tabular crystals, soluble in water, alcohol, and ether, tasting like peppermint, melting at  $51.5^\circ$ , and distilling at  $222-223^\circ$ . This crystalline body is converted by acetic chloride into a diacetate, and is therefore a dihydric alcohol. When boiled in aqueous solution with dilute sulphuric acid, it yields two isomeric limpid oily products, having the composition  $C_8H_{16}O$ , formed therefore from the original substance by abstraction of  $H_2O$ , one of them being a mobile liquid, having a strong camphorous odour, and boiling at  $122-124^\circ$ , while the other is odourless, more viscid, and distils only at  $202-204^\circ$ . The mode of formation of the crystalline dihydric alcohol, and the formation of products containing  $H_2O$  less by treatment with dilute sulphuric acid, is analogous to that of the pinacones. The second crystalline body, likewise having the empirical formula  $C_8H_{18}O_2$ , crystallises in a different system, melts at  $90^\circ$ , and distils at a higher temperature than the first.

H. W.

**Action of Zinc-ethyl on Butyl Chloral.** By K. GARZAROLLI-THURNLACKH (*Annalen*, 213, 369—380; cf. this vol., 824).—By the action of zinc-ethyl on butyl-chloral, ethylene is obtained, together with a white crystalline mass,  $C_3H_4Cl_3.CH_2.OZnEt$ , soluble in ether, and decomposed on treatment with water into ethane, zinc hydroxide, and trichlorobutyl alcohol.

*Trichlorobutyl alcohol*,  $C_4H_7Cl_3O$ , crystallises in prisms, softens at  $56^\circ$ , melts at  $61.5-62^\circ$ , and boils without decomposition at  $120^\circ$ , under 45 mm. pressure. It is readily soluble in alcohol and ether, sparingly in hot water. On treatment with phosphoric chloride, it yields *trichlorobutyl chloride* as a colourless oily liquid boiling at  $85^\circ$  under 10 mm. pressure. Acetic chloride slowly converts the alcohol into *trichlorobutyl acetate*, a liquid of agreeable colour, insoluble in water; boiling at  $131-132^\circ$  under 70 mm. pressure, and having a density of 1.344 at  $8.5^\circ$  (water at  $8.5^\circ = 1$ ). On oxidation with fuming nitric acid, trichlorobutyl alcohol is converted into trichlorobutyric acid, melting at  $58^\circ$ .

*Monochlorocrotyl alcohol*,  $C_4H_7ClO$ , is best prepared by the action of a slight excess of zinc-dust on trichlorobutyl alcohol, melted under 10—15 times its weight of water slightly acidulated with hydrochloric acid. It is a colourless oily liquid, of allyl-like odour, sp. gr. 1.1312, compared with water at the same temperature, and boils at  $158.3^\circ$  under 742.5 mm. pressure; it solidifies to a crystalline mass in a freezing mixture of ice and calcium chloride. On treatment with fuming

nitric acid, it is completely decomposed. By the action of bromine, it yields monochlorodibromobutylalcohol, which, on successive treatment with nitric acid and zinc-dust, yields monochlorocrotonic acid melting at  $97^{\circ}$ . *Monochlorocrotyl acetate* is a colourless mobile liquid, heavier than water, and boiling at  $168\text{--}169^{\circ}$  under  $741\cdot1$  mm. pressure.

A. J. G.

**Ethyl Acetocyanacetate and its Derivatives.** By A. HALLER and A. HELD (*Compt. rend.*, **95**, 235—237).—65 grams of ethyl acetate, prepared by Wislicenus's method, is mixed with the same weight of absolute alcohol, and 10 grams of sodium added in small fragments. When all the sodium has dissolved, a current of pure and dry cyanogen chloride is passed into the liquid until saturated, the reaction being regulated by keeping the flask cool. After saturation with cyanogen chloride, the liquid is diluted with an equal volume of water, neutralised with sodium carbonate, and agitated with ether, in order to remove unaltered acetoacetic ether. The aqueous solution is then acidified with sulphuric acid, and again agitated with ether. The latter on evaporation leaves an orange-yellow liquid, which is purified by distillation in a vacuum. Thus obtained, ethyl acetocyanate,  $\text{CH}_3\text{CO}\cdot\text{CH}(\text{CN})\text{COOEt}$ , forms a mass of small white crystals, with a burning taste and strongly acid reaction. It is only slightly soluble in water, but dissolves in alcohol in all proportions, and liquefies in the vapours of ether, chloroform, carbon bisulphide, and benzene. The alcoholic solution has no action on polarised light. The crystals melt at  $26^{\circ}$ , forming a limpid colourless liquid; sp. gr. at  $19^{\circ} = 1\cdot102$ , which remains in a superfluid condition even at  $-15^{\circ}$ . If cyanogen gas is used instead of cyanogen chloride, the same compound is formed, but the yield is much smaller.

When the ethereal salt is boiled for some time with an excess of potash, ammonia and alcohol are given off, and a residue of potassium acetate and carbonate is left: probably it first splits up into potassium acetate and malonate, the latter being then decomposed by the excess of potash into carbonate and acetate. The same decomposition takes place when it is heated with hydrochloric acid in sealed tubes.

The *sodium* derivative,  $\text{CH}_3\text{CO}\cdot\text{CNa}(\text{CN})\cdot\text{COOEt}$ , is obtained by adding sodium carbonate to an alcoholic solution of the ether. It forms long silky anhydrous needles, soluble in all proportions in water and alcohol.

The *calcium* derivative,  $(\text{C}_7\text{H}_5\text{NO}_3)_2\text{Ca} + 2\text{H}_2\text{O}$ , is obtained in a similar manner. It forms white crystals, derived from a monoclinic prism of  $105^{\circ} 32'$ , slightly soluble in cold water, somewhat soluble in boiling water, very soluble in alcohol. At  $140^{\circ}$ , the crystals lose 2 mols.  $\text{H}_2\text{O}$ , and at a higher temperature they are decomposed.

C. H. B.

**Products of the Decomposition of Ethyl Nitroacetate.** By A. STEINER (*Ber.*, **15**, 1604—1605).—When pure ethyl nitroacetate is boiled it is decomposed, yielding nitric oxide, carbonic anhydride, ethyl oxalate, and a small quantity of alcohol. This fact accounts for the poor yield of this substance which Forcrand (*Compt. rend.*, **88**, 974) obtained by the action of dry silver nitrite on the monobrom-



acetate. More satisfactory results ensue when the ingredients are heated at 120° for not more than 30 minutes. W. C. W.

### Derivatives of Itaconic, Citraconic, and Mesaconic Acids.

By O. STRECKER (*Ber.*, **15**, 1639—1642).—The author does not confirm the statement of Swarts (*Bull. Acad. Roy. Belg.*, 1873, **36**, 34), that ethyl mesaconate is produced in the preparation of ethyl citraconate by the action of alcohol and hydrochloric acid on citraconic acid.

*Citraconic chloride*, obtained by the action of phosphorus pentachloride on citraconic acid, is a colourless liquid of sp. gr. 1.408 at 16.4°, compared with water at the same temperature. It boils at 95°, under a pressure of 17.5 mm.

*Itaconamide* is best prepared by treating methyl itaconate with aqueous ammonia; it forms transparent colourless crystals (m. p. 192°), freely soluble in hot water, and sparingly soluble in alcohol. The amide decomposes at 203°; it is also slowly decomposed by boiling with water.

*Citraconamide*, prepared from methyl citraconate, crystallises in colourless tables, soluble in water. It is slowly decomposed by boiling with water. When heated it begins to decompose at 184°, and melts at 191°, giving off ammonia and forming citraconimide.

*Mesaconamide* forms flat transparent crystals, melting at 176.5°; it decomposes at 200°, and slowly evolves ammonia when boiled with water.

*Itaconanilide*,  $C_5H_4O_2(NHPh)_2$ , described by Gottlieb (*Annalen*, **77**, 265), crystallises in white scales (m. p. 185°), soluble in alcohol and ether.

*Citraconanilide* is precipitated together with aniline hydrochloride, when ethereal solutions of aniline and citraconic chloride are mixed together; the two substances are easily separated by washing with water. The anilide is deposited from an alcoholic solution in white silky needles, soluble in ether; it melts at 175.5°, and at 180° is converted into *citraconanil* (m. p. 96°), which is also formed when a mixture of citraconic acid and aniline is heated at 100°.

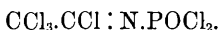
*Mesaconanilide* crystallises in silky white needles (m. p. 185.7°), freely soluble in alcohol and ether, sparingly soluble in boiling water. When mesaconanilide is heated at 268°, it is converted into aniline and citraconanil; aniline mesaconate, heated at 240° yields citraconanil.

W. C. W.

**Action of Chlorine on Amides.** By A. STEINER (*Ber.*, **15**, 1606—1609).—When chlorine is passed into water containing trichloracetamide in suspension, trichloracetochloramide is formed. This substance has been described by Hofmann (*Ber.*, **15**, 407); it is converted into trichloracetamide by the action of ammonia; trichloracetochloramide is not decomposed by potash. When the alcoholic solution is neutralised with alcoholic potash and evaporated, crystals of the potassium salt of trichloracetamide are produced.

Wallach has shown (*Annalen*, **184**, 26) that a body having the composition  $C_2Cl_6ONP$ , is formed by the action of phosphorus pentachloride on trichloracetamide. Since this compound cannot be obtained

when trichloroacetochloramide is substituted for trichloroacetamide, the author concludes that this substance has the constitution

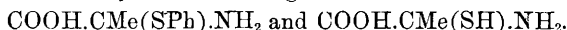


Trichloroacetamide is not attacked by chlorine: Oxamide yields oxalic acid and ammonia when treated with moist chlorine.

W. C. W.

**Phenylmercapturic Acid, Cystine and Serine.** By E. BAUMANN (*Ber.*, **15**, 1731—1735).—Concentrated alcoholic solutions of phenylmercapturic acid and of bromophenylmercapturic acid are feebly laevorotatory. Alkaline solutions of these compounds are dextrorotatory, but alkaline solutions of cystine and bromocystine are laevorotatory.

Phenylmercapturic acid is split up by acids into acetic acid and phenylcystine, and phenylcystine is decomposed by boiling with alkalis into phenyl sulphhydrate, ammonia, and pyrrolic acid. On warming cystine with ammoniacal silver solution, ammonium pyrrolic acid is formed, and when cystine is boiled with baryta-water, it yields oxalic and uric acids. These reactions induce the author to regard phenylcystine and cystine as having the constitutional formulæ



Serine,  $\text{C}_3\text{H}_7\text{NO}_3$ , is slowly decomposed by boiling with baryta-water. Ammonia is evolved, but neither oxalic nor uric acids are produced. A 5 per cent. aqueous solution of serine is optically inactive.

W. C. W.

**Dimethylsulphamic Acid.** By R. BEHREND (*Ber.*, **15**, 1613—1614).—Dimethylamidodimethylsulphuryl chloride is decomposed by warm water with formation of dimethylsulphamic acid and a small quantity of dimethylamine sulphate. Dimethylsulphamic acid,  $\text{NMe}_2.\text{SO}_3\text{H}$ , forms white crystals (m. p.  $165^\circ$ ), soluble in water and hot alcohol. The acid decomposes carbonates, forming salts. Ethyl dimethylsulphamate prepared by the action of dimethylamidodimethylsulphuryl chloride on an alcoholic solution of sodium ethylate, is a yellow oil soluble in alcohol and ether. It is decomposed by heat, but is not attacked by alcoholic ammonia at the ordinary temperature.

W. C. W.

**Substituted Sulphamides and Amidodimethylsulphuryl Chloride.** By R. BEHREND (*Ber.*, **15**, 1610—1613).—A series of substituted sulphamides is formed by the action of ammonia and amines on dimethylamidodimethylsulphuryl chloride,  $\text{NMe}_2.\text{SO}_2\text{Cl}$ . Dimethyldiethylsulphamide,  $\text{NMe}_2.\text{SO}_2.\text{NEt}_2$ , is prepared by adding a solution of diethylamine in chloroform to dimethylamidodimethylsulphuryl chloride; the residue which is left on evaporating the mixture is dissolved in ether, and this solution is washed with water containing hydrochloric acid, afterwards with sodium carbonate, and finally with pure water. On evaporating the ethereal solution, dimethylethylsulphamide remains as a yellow oil (b. p.  $229^\circ$ ) which is heavier than water. The oil is soluble in alcohol, ether, chloroform, and benzene.

Dimethylsulphamide,  $\text{NMe}_2.\text{SO}_2.\text{NH}_2$ , is prepared by passing ammonia into dimethylamidodimethylsulphuryl chloride, and extracting the product

with ether. The sulphamide from the ethereal solution is deposited in prisms melting at  $96^{\circ}$  and soluble in alcohol, ether, and water.

*Dimethylparatolylsulphamide*,  $\text{Me}_2\text{N}.\text{SO}_2.\text{NH}.\text{C}_7\text{H}_7$ , obtained by the action of paratoluidine on dimethylamidodisulphuryl chloride. The crude product is extracted with very dilute hydrochloric acid and the residue is dissolved in alcohol. The addition of water to the alcoholic solution precipitates the sulphamide as a white crystalline mass melting at  $90.5^{\circ}$ , soluble in alcohol, ether, and chloroform. The sulphamide also dissolves in soda solution, forming a crystalline sodium salt. This compound is decomposed by the carbonic acid of the atmosphere.

*Diethylamidodisulphuryl chloride*, obtained by the action of sulphuryl chloride on diethylamine hydrochloride, is a yellow oil (b. p.  $208^{\circ}$ ) resembling the corresponding methyl compound.

When diethylamidodisulphuryl chloride and diethylamine are heated together in sealed tubes at  $60^{\circ}$ , diethylamine hydrochloride and tetrethylsulphamide,  $\text{SO}_2(\text{NEt}_2)_2$ , are produced. The sulphamide is a yellow oil boiling at  $250^{\circ}$ . By passing dimethylamine into diethylamidodisulphuryl chloride, diethyldimethylsulphamide is formed, which is probably identical with the compound produced by the action of diethylamine on dimethylamidodisulphuryl chloride. It boils at  $229^{\circ}$  with partial decomposition.

W. C. W.

**Derivatives of the Three Isomeric Xylenes.** By B. RADZISZEWSKI and P. WISPEK (*Ber.*, 15, 1743—1748).—When paraxylene, prepared from paradibromobenzene by V. Meyer's method, is acted on by bromine-vapour, *paraxylyl bromide*,  $\text{C}_6\text{H}_4\text{Me}.\text{CH}_2\text{Br}$ , is obtained in colourless needles (m. p.  $31^{\circ}$ , b. p.  $220^{\circ}$ ), soluble in boiling ether, chloroform, and alcohol. *Paraxylylene bromide*,  $\text{C}_6\text{H}_4(\text{CH}_2\text{Br})_2$ , obtained as a bye-product in the preparation of the preceding compound, crystallises in colourless plates (m. p.  $140^{\circ}$ , b. p.  $240$ — $250^{\circ}$ ), soluble in boiling chloroform; 100 parts of ether at  $20^{\circ}$  dissolve only 2.65 parts of the dibromide. When the nitrile, prepared by the action of potassium cyanide on paraxylyl bromide, is decomposed by potash, *paratolylacetic acid*,  $\text{C}_6\text{H}_4\text{Me}.\text{CH}_2.\text{COOH}$ , is produced. This acid forms colourless needles or plates melting at  $89^{\circ}$ , soluble in hot water. The following salts were prepared:— $\text{C}_6\text{H}_5\text{AgO}_2$ , deposited from a hot aqueous solution in glistening needles;  $(\text{C}_6\text{H}_5\text{O}_2)_2\text{Ca} + 3\text{H}_2\text{O}$ , silky needles. The lead, copper, and ferric salts are amorphous, and insoluble in water.

*Ethylparaxylyl ether*,  $\text{C}_6\text{H}_4\text{Me}.\text{CH}_2.\text{OEt}$ , is a colourless liquid boiling at  $203^{\circ}$ ; sp. gr. at  $17^{\circ} = 0.9304$ .

*Metaxylyl bromide* is a strongly refractive liquid boiling at  $215^{\circ}$ ; and having a density of 1.3711 at  $23^{\circ}$ .

*Metaxylylene bromide* resembles the para-compound in crystalline form, and in its melting and boiling points. It dissolves easily in hot chloroform; 100 parts of ether at  $20^{\circ}$  dissolve 2.3 parts of the dibromide. On oxidation with chromic mixture, it yields isophthalic acid. *Metatoluic acid* forms lustrous needles melting at  $54^{\circ}$ , sparingly soluble in cold water. The silver, calcium, lead, and copper salts resemble the corresponding para-compounds. *Ethylmetaxylyl ether* is

a colourless liquid boiling at  $202^{\circ}$ , and having a sp. gr. of 0.9302 at  $17^{\circ}$ ). *Metaxylyl alcohol*,  $C_6H_4Me.CH_2.OH$ , boils at  $215^{\circ}$ , and has a sp. gr. of 0.9157 at  $17^{\circ}$ .

*Orthoxylyl bromide* boils at  $216^{\circ}$ . Its sp. gr. is 1.3811 at  $23^{\circ}$ . *Orthoxylylene bromide* is deposited from chloroform in flat prisms (m. p.  $143^{\circ}$ , b. p.  $240-250^{\circ}$ ): 2.07 parts of this compound dissolve in 100 parts of ether at  $23^{\circ}$ . *Orthotoluylacetic acid* crystallises in silky needles melting at  $85^{\circ}$ , freely soluble in hot water. The silver salt is deposited from hot water in plates.  $Ca(C_9H_9O_2)_2 + 4H_2O$  forms silky needles. The lead, copper, and ferric salts resemble the corresponding para- and meta-compounds. W. C. W.

**Amidoethylbenzene and Ethylorthamidotoluene.** By G. BENZ (*Ber.*, 15, 1646—1652).—The chief product of the action of ethyl alcohol on aniline zinc chloride at  $280^{\circ}$  is paramidoethylbenzene. This compound has been described by A. W. Hofmann (*Ber.*, 7, 527), who obtained it from ethylaniline hydrochloride, and also by Beilstein and Kuhlberg (*Annalen*, 156, 208).

*Ethylorthamidotoluene*,  $NH_2.C_6H_3MeEt$ , is prepared by heating equal molecules of ethyl alcohol, orthotoluidine, and zinc chloride at  $270^{\circ}$  for eight hours. The crude product is dissolved in hydrochloric acid, and the base liberated in the form of an oily liquid by the addition of soda to the solution. The portion of the oil boiling between  $220^{\circ}$  and  $250^{\circ}$  was converted into oxalate, and purified by recrystallisation from hot water: an excess of oxalic acid must be avoided as it increases the solubility of the salt. The pure base is a colourless oil boiling at  $229^{\circ}$  and miscible with alcohol and ether.

The *acetic* derivative,  $C_9H_{12}AcN$ , is deposited from alcohol in long silky needles soluble in benzene and alcohol. It melts at  $105^{\circ}$  and boils at  $314^{\circ}$ . The *sulphate*,  $(C_9H_{13}N)_2.H_2SO_4$ , forms white glistening needles or plates soluble in warm water. The *oxalate*,  $(C_9H_{13}N)_2.H_2C_2O_4$ , forms white scales sparingly soluble in alcohol, ether, and cold water. W. C. W.

**Amidoamylbenzene.** By A. CALM (*Ber.*, 15, 1642—1646).—When a mixture of amyl alcohol (1 mol.) and aniline (2 mols.) is heated with zinc chloride (1 mol.) at  $270^{\circ}$ , amidoamylbenzene,  $NH_2.C_6H_4.C_5H_{11}$ , is produced. This compound is identical with the base which Hofmann (*Ber.*, 10, 528) obtained by heating secondary amylaniline hydrochloride.

By the action of sodium nitrite on a warm dilute solution of amidoamylbenzene hydrochloride, a phenol is produced (b. p.  $247-251^{\circ}$ ), which resembles the amylphenol obtained by Liebermann (*Ber.*, 15, 156) by the action of zinc chloride on phenol and amyl alcohol. W. C. W.

**Conditions of Formation of Rosanilines.** By A. ROSENSTIEHL and M. GERBER (*Compt. rend.*, 95, 238—239).—With reference to the production of rosaniline, the amines may be divided into three classes. The first class includes *paratoluidine*,  *$\alpha$ -metaxylylidine*, and *mesidine*, which yield no trace of red colouring matter when heated with arsenic acid either alone or mixed with one another, but yield magenta under

ordinary manufacturing conditions when mixed with members of the second class. All the members of the first class contain the  $\text{CH}_3$  group in the para-position, and this furnishes the carbon necessary to unite the three aromatic amine residues into the triphenyl-methane group characteristic of rosanilines. The second class includes *aniline*, *orthotoluidine*, and  *$\gamma$ -metaxylydine* which, alone or mixed with one another, yield no magenta when heated with arsenic acid. The authors find, however, that orthotoluidine even when purified as carefully as possible, yields appreciable quantities of magenta when heated alone with arsenic acid, and that treatment with successive fresh quantities of arsenic acid results in the formation of successive quantities of magenta. It would appear, therefore, either that orthotoluidine retains small quantities of paratoluidine or  $\alpha$ -metaxylydine with unusual obstinacy, or that the high temperature which it is necessary to employ produces partial molecular change. The third class includes *metatoluidine* and *symmetrical xylydine* which yield no magenta, even when mixed with members of the preceding group.

The authors confirm the conclusion of E. and O. Fischer, that the presence of a para-derivative is absolutely essential to the formation of magenta under ordinary manufacturing conditions. C. H. B.

**Action of Sulphuretted Hydrogen on Diazobenzene.** By C. GRAEBE and W. MANN (*Ber.*, 15, 1683).—Phenyl sulphide may be easily prepared by the action of sulphuretted hydrogen or, preferably, ammonium sulphide, on a solution of diazobenzene in hydrochloric or sulphuric acids. A reddish-yellow explosive precipitate is formed which gradually decomposes at the ordinary temperature with evolution of nitrogen and formation of an oily liquid. In order to avoid explosion, the operation is carried on in a large basin containing lumps of ice. The oily product is collected, separated from precipitated sulphur, boiled for two hours, and distilled, when the phenyl sulphide comes over at  $291^\circ$ . W. C. W.

**Orcinoldiazotoluene.** By S. SCICCHILONE (*Gazzetta*, 12, 223).—On mixing a solution of 45 grams of potassium nitrite in 3 litres of water with one of 30 grams toluidine nitrate and 30 of orcinol in 1500 c.c. water, a copious red precipitate is formed almost instantaneously; the *orcinoldiazotoluene*,  $\text{C}_7\text{H}_7\text{N}_2\cdot\text{C}_6\text{H}_2\text{Me}(\text{OH})_2$ , was obtained in microscopic reddish-brown crystals (m. p.  $203\text{--}206^\circ$ ) from boiling alcohol, but is decomposed with formation of a resin by repeated crystallisation, whether from alcohol or other solvents. In only one instance, however, has the author been able to crystallise the diazo-compound; in other preparations, a few seconds' boiling with alcohol was sufficient to alter it. C. E. G.

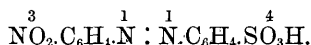
**Nitro-derivatives of Azobenzene-para-sulphonic Acid.** By J. V. JANOVSKY (*Monatsh. Chem.*, 3, 504—509).—The mononitro-acid which the author obtained a short time ago by the action of nitric acid on azobenzene-monosulphonic acid (p. 836 of this volume) appears on further investigation to be a mixture of two isomeric acids, the forma-

tion of which is accompanied by that of a dinitro- and a trinitro-acid.

*Mononitrazobenzene-para-sulphonic Acid*.—To prepare these acids, azobenzene-*p*-sulphonic acid,  $\text{C}_6\text{H}_5\cdot\overset{1}{\text{N}}_2\cdot\overset{4}{\text{C}_6\text{H}_4}\cdot\overset{3}{\text{SO}_3\text{H}}$ , is treated with 10 to 12 times its volume of nitric acid (sp. gr. 1.41), the solution being heated to the boiling point, and diluted after about 15 minutes. The dilute solution is then evaporated to dryness on the water-bath, and the excess of nitric acid removed by dissolving the residue in water and further evaporation. If the mixture of nitro-acids thus obtained be treated with water, the greater part dissolves, while a small portion remains undissolved.

The sparingly soluble mononitro-acid (A) resembles the monosulphonic acid itself, and like the latter separates from a hot solution in laminæ having a golden lustre. It is moderately soluble in dilute nitric acid, very sparingly in cold water, and crystallises in rhombic plates. Its *potassium salt*,  $\text{C}_{12}\text{H}_8\text{NO}_2\cdot\text{SO}_3\text{K}$ , crystallises in large, nearly colourless laminæ.

The easily soluble mononitro-acid (B) yields, on evaporation and subsequent crystallisation, a mass of microscopic laminæ. It is distinguished from the former acid by the dark colour of its solutions and of those of its salts. By reduction this acid yields an amidobenzene-sulphonic acid, which by further reduction is converted into paramidobenzene-sulphonic (sulphanilic) acid and metaphenylenediamine: hence the formula of the B-nitro-acid is



The mother-liquors of the salts of this acid deposit deep yellow-red salts, probably belonging to a third isomeric acid not yet investigated.

The *potassium salt* of the B-nitro-acid crystallises in anhydrous orange-red rhombic plates having the form of those of sulphanilic acid, and very slightly soluble in water. The *sodium salt* crystallises in easily soluble rhombic laminæ. The *lead salt*,  $(\text{C}_{12}\text{H}_8\text{NO}_2\cdot\text{N}_2\cdot\text{SO}_3)_2\text{Pb}$ , crystallises from hot water in shining needles, sparingly soluble in cold water. The *barium salt*,  $(\text{C}_{12}\text{H}_8\text{NO}_2\cdot\text{N}_2\cdot\text{SO}_3)_2\text{Ba}$ , crystallises readily from hot water in orange-yellow microcrystalline prisms.

The B-*amido-acid*, already mentioned as obtained by partial reduction of the B-nitro-acid, is interesting as being isomeric with the aniline-yellow produced from diazobenzene-sulphonic acid: it will be more fully described in a future communication.

*Dinitrazobenzene-para-sulphonic acid*,  $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ , is formed by treating azobenzene-para-sulphonic acid at  $100^\circ$  with 10 parts of nitric acid of sp. gr. 1.45. On diluting the resulting liquid and evaporating, there remains a crystalline mass mostly soluble in water; and on exhausting this with boiling water, there remains a resinous body soluble in alcohol, which contains nitrogen as  $\text{NO}_2$ , but no sulphur, and therefore cannot be a sulphonic acid. It resembles the product obtained by the nitration of azobenzene, and appears to be produced by a more complete decomposition of the sulphonic acid.

The solution obtained by the action of boiling water on the crystalline mass above mentioned yields the dinitro-acid on evaporation, in the form of stellate groups of microscopic needles. This acid is easily soluble in water, very hygroscopic, and has an orange-yellow colour, lighter than that of the mononitro-acid. By reduction, it yields sulphanilic acid and triamido-benzene. Its *potassium salt* crystallises in thick flat yellow needles,  $C_{12}H_7(NO_2)_2.N_2.SO_3K$ , which detonate violently when heated. It is less soluble than the potassium salt of the mononitro-acid. The *barium salt* separates from boiling water in warty groups of microscopic needles, 1 part of which dissolves in 140 parts water at  $68^\circ$ . The *lead salt* crystallises in warty groups of yellow needles. The *silver salt* is yellow, pulverulent, explosive, and very sparingly soluble.

*Trinitrazobenzene-sulphonic acid*,  $C_{12}H_6(NO_2)_3.N_2.SO_3H$ , is formed by heating the monosulphonic acid with nitric acid of sp. gr. 1.48 to 1.51; and on treating the product with hot water, a resinous body insoluble in water and in alcohol separates out, and the solution when evaporated yields the trinitro-acid as a crystalline mass composed of stellate groups of microscopic laminæ. The *barium salt* is sparingly soluble in water, and crystallises in nodular masses of a light yellow colour. The *lead salt* is also light yellow. The *sodium salt* is likewise light yellow, but very soluble. The *silver salt* is yellow, microcrystalline, and very explosive.

H. W.

**Preparation of Triphenylphosphine.** By A. MICHAELIS and A. REESE (*Ber.*, 15, 1610).—Triphenylphosphine can be prepared by adding slices of sodium to a mixture of phosphorous chloride (1 mol.) and bromobenzene (3 mols.), diluted with four times its volume of ether. The flask in which the operation is conducted is cooled with water, and is also provided with an upright condenser. After 12 hours, the mixture is warmed, the ether decanted, and the residue shaken up with ether. The residue which remains on distilling the ethereal solution consists of triphenylphosphine: it may be purified by recrystallisation from hot alcohol.

W. C. W.

**Orthanisidine-derivatives.** By F. HEROLD (*Ber.*, 15, 1684—1687).—*Orthanisidine platinochloride*,  $(MeO.C_6H_4.NH_2.HCl)_2.PtCl_4$ , is an unstable compound. *Monochloranisidine*,  $MeO.C_6H_3Cl.NH_2$ , is obtained as a bye-product in the manufacture of anisidine by the reduction of orthonitranisole with tin and hydrochloric acid. It is contained in the residue after the anisidine has been distilled over in a current of steam. This substance melts at  $52^\circ$ , and boils at  $260^\circ$ . It crystallises in white needles or prisms, soluble in alcohol, ether, and benzene. The hydrochloride forms colourless needles, which rapidly acquire a pale green tint. It is soluble in alcohol and water. The *platinochloride*,  $(MeO.C_6H_3Cl.NH_2.HCl)_2.PtCl_4$ , crystallises in yellow needles, soluble in water and alcohol, but insoluble in ether. The picrate forms greenish-yellow needles, soluble in alcohol and ether. It melts at  $200^\circ$  with decomposition.

The acetic-derivative,  $MeO.C_6H_3Cl.NHAc$ , crystallises in plates,

which melt at  $150^{\circ}$  and boil at  $326^{\circ}$ . *Mononitracetochloranisidine*, prepared by adding fuming nitric acid to a solution of the preceding compound in glacial acetic acid, forms pale yellow needles melting at  $185^{\circ}$ , soluble in alcohol, ether, and glacial acetic acid. The *dinitro-derivative*, obtained by dissolving dry acetochloranisidine in fuming nitric acid, crystallises in needles melting at  $165^{\circ}$ ). The *trinitro-compound* forms orange-coloured needles melting at  $198^{\circ}$ , soluble in alcohol and strong acetic acid. The *thiocarbamide*, prepared by the action of carbon bisulphide and alcohol on chloranisidine, crystallises in white needles melting at  $152.5^{\circ}$ , soluble in alcohol, ether, and acetic acid. By the action of nitrous acid on chloranisidine, chlor-anisoil (b. p.  $193^{\circ}$ ) appears to be formed. W. C. W.

**Condensation-products of Phenols and Acetic Acid, and a Simple Method for the Preparation of the Ethereal Salts of Phenols.** By F. RASINSKI (*J. pr. Chem.* [2], 26, 53—66).—This work is a continuation of Nencki and Silber's researches (Abstr., 1881, 591, 811). Gallacetophenone gives rise to a colouring matter when heated with zinc chloride, in the same way that resacetophenone does. This colouring matter dissolves in acids with a yellow, and in alkalis with a violet colour; it is extremely unstable. The alkaline solution, like that of pyrogallol, turns brown in the air. *Phenacetein*,  $C_{16}H_{12}O_3$ , is prepared by boiling together phenol (10 grams), acetic anhydride (20 grams), and zinc chloride (20 grams) for 20—30 minutes; the product is well washed with water, dissolved in dilute hydrochloric acid, and as soon as the resinous matter is deposited the solution is filtered and the colouring matter precipitated by ammonia. It is an amorphous carmine-red powder, easily soluble in alcohol, ether, glacial acetic acid, and alkalis, less so in chloroform and carbon bisulphide, and insoluble in water and benzene. The acid solution is yellow, the alkaline raspberry-red: the colour is fugitive. With acetic anhydride, phenacetein forms an *acetate*, crystallising in dark red prisms, soluble in alcohol and glacial acetic acid with green colour. *Orcacetein*,  $C_{18}H_{16}O_4$ , is obtained when orcinol (10 grams), glacial acetic acid (15 grams), and zinc chloride (20 grams) are heated to the boiling point of the mixture. The product is washed well with water and dissolved in dilute alcohol. A small quantity of some yellow prisms of a homologue of acetofluorescein are deposited from the solution. The chief product remains dissolved, and the filtered solution after being evaporated, is treated with ethyl acetate, ether is added, and the resinous precipitate is filtered off: the residue left on evaporating the ethereal solution is washed with dilute ammonia, dissolved in potash, and precipitated with hydrochloric acid. Orcacetein is a yellow amorphous powder, easily soluble in ether, alcohol, and glacial acetic acid, sparingly so in chloroform, carbon bisulphide, and dilute ammonia, and insoluble in water and benzene. Its alkaline solutions are yellow, with slight green fluorescence. Orcacetein does not yield a crystalline acetate with acetic anhydride, but resacetein under similar circumstances yields a *resacetein triacetate*,  $C_{16}H_9Ac_3O_4$ , crystallising from glacial acetic acid in red tables with golden lustre (m. p. calc.  $229^{\circ}$ ), not soluble in alkalis without decomposition. When



phosphorus oxychloride is added to a solution of orcinol in glacial acetic acid, the product poured into water, decomposed by boiling with dilute alkali, and the solution filtered, the addition of hydrochloric acid precipitates a substance crystallising in silky needles (m. p.  $146^{\circ}$ ), easily soluble in alkalis, alcohol, ether, and glacial acetic acid, less so in water, benzene, and carbon bisulphide. Ferric chloride colours the aqueous solution deep black, which on boiling disappears, with formation of a brown precipitate. This substance is probably *orcinyll monacetate*,  $C_7H_7\overline{Ac}O_2$ . At the same time small quantities of *orcacetophenone*,  $C_9H_{10}O_3$  (b. p.  $284-286^{\circ}$ ) are produced. By boiling orcinol with acetic anhydride, *orcinyll diacetate*,  $C_7H_6(\overline{Ac}O)_2$ , is obtained, boiling at  $280-284^{\circ}$ . The reaction with phosphorus oxychloride shows that, in the presence of this reagent, phenols can combine with acids, with elimination of water and formation of acid ethereal salts; it is therefore a general reaction. *Phenyl benzoate* can be prepared by adding phosphorus oxychloride to a fused mixture of benzoic acid and phenol heated to between  $106-120^{\circ}$ , as long as hydrochloric acid is evolved. It is purified by washing with dilute potash and crystallising from alcohol. Its properties, &c. (m. p.  $69^{\circ}$ ), are those given by Malin (*Annalen*, **137**, 78) and Doebner (*Ber.*, **13**, 2222; *Abstr.*, 1881, 165).

By this method the following substances have been prepared:—*Phenol succinate*,  $PhO\cdot\overline{Su}\cdot PhO$  (m. p.  $119^{\circ}$ ); *resorcinyll benzoate* (m. p.  $117^{\circ}$ ) and *succinate* (the author could not prepare fluoresceine and eosine succinates from this ethereal salt); *orcinyll benzoate* (m. p.  $88^{\circ}$ ), *succinate*, and *oxalate*. From anhydrous ethyl alcohol, a yellowish-red liquid, lighter than water, with an odour of phenetol. Corresponding ethereal salts are obtained from glycerol and acetic and benzoic acids, also from glycerol and phenol. D. A. L.

**Resocyanin, and the Action of Ethyl Acetoacetate on the Phenols in Presence of Dehydrating Agents.** By M. WITTENBERG (*J. pr. Chem.* [2], **26**, 66—78).—The author finds that resocyanin (*J. pr. Chem.*, **24**, 125) yields resorcinol when fused with potash. W. Schmid (*ibid.* [2], **25**, 81; this vol., 509) found that resocyanin is formed when ethyl acetoacetate and resorcinol are heated with zinc chloride; and since then it has been shown that the same result is obtained with other substances besides zinc chloride, viz., phosphorus oxychloride, benzotrichloride, and concentrated sulphuric acid, the last-mentioned giving the best results. In the paper, the author describes the products of the action of sulphuric acid on ethyl acetoacetate and pyrogallol, and ethyl acetoacetate and orcinol.

Pyrogallol (3 parts) is dissolved in ethyl acetoacetate (2 parts), gently warmed on a water-bath, and mixed with a small quantity of concentrated sulphuric acid; the mass becomes yellow, froths up, and finally solidifies; the product is then washed with water, and crystallised from boiling water. This substance, called *allylene-digallein*,  $C_{15}H_{12}O_6$ , crystallises in rhombic scales and leaflets (m. p.  $235^{\circ}$  uncorr.), containing water of crystallisation which is given off at  $110^{\circ}$ . It is insoluble in cold water, sparingly soluble in benzene, ether, and cold

alcohol, but easily in hot alcohol. Even in very dilute solutions allylene-digallein gives a green colour with ferric chloride; with lead acetate, a lemon-yellow gelatinous precipitate; with barium hydroxide, a gelatinous blood-red precipitate which, when warmed, changes into yellow feathery tufts of needles, and dissolves in alkalis with a yellow-red colour, gradually becoming darker on exposure to the air. Allylene-digallein is much more stable than pyrogallol. By boiling with acetic anhydride, *allylene-digallein diacetate*,  $C_{15}H_{10}O_4(OAc)_2$ , is formed; it crystallises from alcohol in large, colourless, transparent crystals, which melt at  $176^\circ$ , and are insoluble in water, slightly soluble in cold, easily in hot alcohol. In an equally simple manner, a substance is obtained from orcinol in the form of needles (m. p.  $249^\circ$ ) with  $1\frac{1}{2}$  or 2 mols.  $H_2O$ ; the results of analysis correspond with either  $C_{17}H_{16}O_5$  or  $C_{31}H_{30}O_9$ . This substance is insoluble in water, sparingly in cold, easily in hot alcohol and in alkalis, forming a pale yellow solution. The *acetate*,  $C_{17}H_{15}AcO_5$  or  $C_{31}H_{28}Ac_2O_9$ , crystallises in slender white needles (m. p.  $200^\circ$ ); the *bromide*,  $C_{17}H_{13}Br_3O_5$  or  $C_{31}H_{24}Br_6O_9$ , forms four-sided tables. When resocyanin is prepared from resorcinol and citric acid, the chief bye-products are water and carbonic oxide.

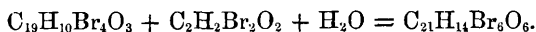
Pyrogallol is dissolved in pure acetone, and a few drops of phosphorus oxychloride added (sulphuric acid does not answer in this case). The product,  $C_9H_{10}O_3$ , is crystalline, does not melt, but turns brown at  $250^\circ$ , and is easily soluble in alcohol and ether, but insoluble in water. The author calls it *gallacetoin*; with alkalis it forms a brown-yellow coloration, which quickly becomes dark. Ferric chloride gives a purple-red (at first deep, afterwards faint). Lead acetate produces a green precipitate, which on shaking becomes blood-red. An alcoholic solution of the substance diluted with water reduces silver nitrate. When boiled with acetic anhydride, it forms *gallacetoin monacetate*,  $C_9H_9AcO_3$ , which crystallises in leaflets.

D. A. L.

**Constituents of Corallin.** By C. ZULKOWSKY (*Monatsh. Chem.*, **3**, 465—485).—According to Dale and Schorlemmer (*C. J.*, 1879, Trans., 148), the product obtained by adding aurin to bromine, both dissolved in glacial acetic acid, is pure tetrabromaurin. Zulkowsky, on the other hand, finds that the bromination of aurin always yields a mixed product consisting of at least two bodies, viz., (1) bronze-coloured crystals; (2) colourless or faintly reddish scales. The bronze-coloured compound appears to be a *hydrobromide of bromaurin*, as it gives off hydrogen bromide in a vacuum at  $100^\circ$ , and more quickly at the temperature of boiling fusel-oil. Treated with water on a filter, it gave up hydrogen bromide (12.04 p.c. bromine), and when the washed precipitate was repeatedly boiled with alcohol, a residue was obtained exhibiting the composition 32.87 to 32.40 p.c. carbon, 1.99 to 1.86 hydrogen, and 56.10 bromine.

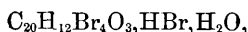
From these results, the author infers that the bronze-coloured compound has the composition  $C_{19}H_{10}Br_4O_3 \cdot 2HBr$ , and that the substance obtained from it by successive treatment with water and boiling alcohol is  $C_{19}H_{10}B_4O_3 \cdot HBr + H_2O$ . These formulæ must, however, be regarded not as finally settled, but merely as affording a provisional explanation of the experimental results.

The second or colourless body produced by the action of bromine on aurin dissolved in acetic acid, and found in the last fractions of the product, is insoluble in water, but dissolves in alcohol with pale-green colour, and does not give up hydrobromic acid to hot water. Its analysis gave numbers agreeing with the formula  $C_{21}H_{14}Br_6O_6$ . The increased proportion of carbon seems to indicate that the acetic acid has taken part in its formation; this may perhaps be represented by the equation:



*Methylaurin and Bromine.*—The bromination of this compound takes place very easily and with great precision. To 2 pts. bromine dissolved in glacial acetic acid is added a solution of 1 pt. methylaurin in a quantity of the same solvent sufficient to prevent crystallisation, the whole being kept cool, and the resulting liquid placed in a basin under a bell-jar to prevent the escape of free bromine. After a while, crystals of considerable size and brassy lustre separate in nearly theoretical quantity, and on filtering, washing with glacial acetic acid, and further concentrating the filtrate, a very small quantity of the same crystals is obtained, traversed by colourless scaly crystals. If the liquids are more concentrated and not kept cool during the bromination, the first products are contaminated either with unaltered methylaurin, or with the colourless crystals above mentioned. The bromine derivative thus obtained is insoluble in cold water, and is decomposed by hot water, which abstracts hydrobromic acid. It dissolves very slightly in alcohol, with brownish-yellow colour.

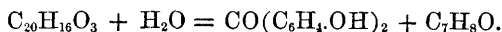
The product, freed from hydrobromic acid by washing with water, dissolves in alcohol with violet colour, in caustic potash with magenta colour, agreeing in these characters with the brominated compound obtained from aurin. It is a *hydrobromide of methylaurin*,



which further resembles the analogous aurin-compound in forming with alcoholic potash a salt which easily separates in distinct metallically lustrous crystals, and dissolves in water with violet colour. After treatment with hot water till it no longer gave the reaction of hydrobromic acid, the residue gave by analysis numbers agreeing with the formula of *tetrabromomethylaurin*,  $C_{20}H_{12}Br_4O_3$ .

*Methylaurin with Potash.*—The product obtained by fusing methylaurin with potassium hydroxide consists mainly of para-hydroxybenzoic acid. Corallin similarly treated yields the same product, together with a small quantity of phenol.

Methylaurin heated with water in sealed tubes at 240—250° is converted into dihydroxybenzophenone and cresol:



*Corallin-phthalein*, the isomeride of phenol-phthalein,  $C_{20}H_{14}O_4$ , which Zulkowsky formerly obtained by the action of oxidising agents on corallin, yields, by fusion with potash, a small quantity of para-

hydroxybenzoic acid, together with a large quantity of resinous matters.

*Nature of the so-called "Oxidised Aurin."*—This easily crystallisable but unstable compound, which the author formerly obtained from corallin, is converted by nascent hydrogen, or by prolonged boiling with dilute alcohol, into leucaurin. From its solution in acid sodium sulphite, hydrochloric acid throws down aurin sulphite in small cubes. Its reactions with reducing agents appear to begin in the manner shown by the equation  $C_{19}H_{16}O_8 = C_{19}H_{14}O_3 + O_2 + H_2O$ , that is to say, it behaves like a hydrated peroxide.

The author therefore endeavoured to prepare it directly from aurin by adding potassium manganate to a solution of that substance in potash. The resulting liquid yielded with sulphuric acid a cinnamon-brown precipitate, from the alcoholic solution of which the "oxidised aurin" crystallised out. This substance, however, when treated with water, easily gives up sulphuric acid; it is in fact a sulphate of aurin, and may also be prepared by adding sulphuric acid to an alcoholic solution of aurin, whereby a cake of needle-shaped crystals is obtained, which may be freed from mother-liquor by pump-filtration and washing. The compound thus prepared is identical in properties and composition with that which is obtained from corallin. When aurin sulphate is dissolved in glacial acetic acid at the boiling heat, red crystals are obtained, consisting of an acetosulphate of aurin.

*Methylaurin sulphate* may be prepared in the same manner as the aurin compound, but takes longer to crystallise. It forms fine crystals of a deep red colour with blue surface-shimmer, which easily give up their sulphuric acid when washed with hot water. It contains 12.96 p.c.  $H_2SO_4$  or 4.23 p.c. sulphur, agreeing with the formula  $(C_{20}H_{16}O_3)_2, H_2SO_4$ .  
H. W.

**Homologues of Deoxybenzoin and Benzophenone.** By C. SÖLLSCHER (*Ber.*, 15, 1680—1682).—*Ethyldeoxybenzoin*,



prepared by the action of aluminium chloride on ethylbenzene and phenylacetic chloride, crystallises in small plates, melting at  $64^\circ$ , freely soluble in ether, benzene, and warm alcohol. On oxidation, it yields terephthalic acid; and on reduction with phosphorus and hydriodic acid at  $190^\circ$ , it yields para-ethyldibenzyl (b. p.  $294^\circ$ ). When treated with alcoholic potash at  $150^\circ$ , it is converted into the secondary alcohol,  $CH_2Ph.CH(OH).C_6H_4Et$ , which boils at a temperature above  $350^\circ$ . By the action of dilute sulphuric acid on this alcohol, ethylstilbene,  $CHPh:CH.C_6H_4Et$ , is obtained, crystallising in plates (m. p.  $90^\circ$ ), soluble in ether, benzene, and boiling alcohol. The addition of bromine to a solution of ethyldeoxybenzoin in ether, gives rise to an addition-product,  $C_{16}H_{14}Br_2O$ , which crystallises in plates (m. p.  $113^\circ$ ), soluble in hot alcohol.

When aluminium chloride acts on metaxylene and phenylacetic chloride, a yellow oil is produced, which, in the course of time, deposits a small quantity of *dimethyldeoxybenzoin*,  $CH_2Ph.CO.C_6H_3Me_2$ , in crystals, melting at  $93^\circ$ , and soluble in ether and hot alcohol. The

chief portion of the ketone remains liquid. It boils without decomposition above  $350^{\circ}$ , and yields  $\alpha$ -xylic acid on oxidation.

*Ethylbenzophenone*,  $\text{PhCO.C}_6\text{H}_4\text{Et}$ , boils above  $300^{\circ}$ , without decomposition. It is heavier than water and dissolves in alcohol, benzene, and ether. It yields parabenzoylebenzoic acid on oxidation, and on reduction with hydriodic acid and phosphorus, it yields the hydrocarbon  $\text{C}_{15}\text{H}_{16}$ , which J. T. Walker obtained from ethylbenzene and benzyl chloride.

*Dimethylbenzophenone*,  $\text{PhCO.C}_6\text{H}_3\text{Me}_2$ , prepared from metaxylene and benzoic chloride, is a liquid heavier than water; it boils above  $350^{\circ}$ . On reduction, it yields a hydrocarbon,  $\text{C}_{15}\text{H}_{16}$ , boiling at  $290^{\circ}$ .

W. C. W.

**Aqueous Solutions of Salicylic Acid.** By W. ALEXEJEFF (*J. pr. Chem.* [2], **25**, 518—521).—Solutions of the acid are obtained by heating the acid with water in closed tubes slightly above  $100^{\circ}$ . When they are cooled quickly, the whole becomes a crystalline magma, but when they are cooled slowly, peculiar results are obtained, the acid separating sometimes as an oil and sometimes in crystals. A few examples of these results are given: solutions containing 73.01 and 66.71 per cent. of the acid solidify suddenly respectively at  $68^{\circ}$  and  $67^{\circ}$ ; whilst those containing 61.2, 42.90 to 21.20, or 4.57, become turbid at  $76^{\circ}$ ,  $90.5^{\circ}$ , or  $63^{\circ}$ , and deposit the acid as an oil: solutions containing 2.96 per cent. become turbid at  $49^{\circ}$ , and the acid separates in crystals: solutions made at  $12.5^{\circ}$  contain 0.16 per cent. of salicylic acid; at  $66^{\circ}$ , 1.27 per cent.; at  $81^{\circ}$ , 2.44 per cent.; at  $100^{\circ}$ , 8.67 per cent. From these facts, the author infers that there are three different kinds of solutions, viz.:—1st. Solutions of water in salicylic acid. 2nd. Solutions of the acid in water, which deposit, on cooling, the “liquid acid.” 3rd. Solutions of the acid in water depositing, under similar conditions, crystals of the acid. The “liquid acid” is an example of the 1st kind, and the supernatant liquid, which is highly refractive, of the 2nd or 3rd; for the same solution may be classed in either one of these according to the temperature at which it is prepared, inasmuch as all solutions made below  $100^{\circ}$  contain the “solid acid,” whilst those made above  $100^{\circ}$  contain the “liquid acid.”

D. A. L.

**Two Anhydrides of Parahydroxybenzoic Acid.** By A. KLEPL (*J. pr. Chem.* [2], **25**, 525—526).—When parahydroxybenzoic acid is distilled, about half of it breaks up into phenol and carbonic anhydride; the remainder consists of anhydrides, water, and a substance of the constitution  $\text{C}_{13}\text{H}_{10}\text{O}_3$ . In order to obtain satisfactory results, overheating must be avoided, and the distillation ought to be stopped as soon as the residue becomes solid. This residue consists of a mixture of two anhydrides; one soluble, the other insoluble in absolute alcohol. The *insoluble anhydride*,  $\text{C}_7\text{H}_4\text{O}_2$ , preponderates, amounting to about one-third of the acid used. It is a white amorphous powder, insoluble in ordinary solvents; when heated, it decomposes without melting. It dissolves in concentrated sulphuric acid, forming parahydroxybenzosulphonic acid. By prolonged boiling

with potash, this anhydride is reconverted into parahydroxybenzoic acid. When heated in a sealed tube with dilute sulphuric acid, it is decomposed, producing carbonic anhydride and phenol. The *soluble anhydride*,  $C_{21}H_{14}O_7$ , is deposited from the boiling alcoholic solution as it cools as a white, indistinctly crystalline, powder melting at about  $275^\circ$ . It is produced from 3 mols. parahydroxybenzoic acid by the splitting off of 2 mols. water. It is easily reconverted into the acid, even by warming it with dilute alkalis, and, when etherified, forms ethereal salts of parahydroxybenzoic acid. When warmed with acetic anhydride, it dissolves, forming an *acetate*,  $C_{21}H_{13}O_7\overline{Ac}$ , which crystallises in small needles melting at  $230^\circ$ . D. A. L.

**Some Derivatives of Isophthalic Acid.** By B. BEYER (*J. pr. Chem.* [2], **25**, 465—518).—After a short historical sketch of work done by various workers in connection with this subject, the author describes his own experiments. The isophthalic acid used was prepared by Fittig's method (*Annalen*, **153**, 268), by the oxidation of coal-tar xylene with potassium dichromate and sulphuric acid, and separation of the mixture of terephthalic and isophthalic acids thus obtained by means of their barium salts.

*$\gamma$ -Mononitroisophthalic acid*,  $NO_2.C_6H_3(COOH)_2 + 1\frac{1}{2}H_2O$  (m. p.  $249^\circ$ ), is prepared by heating isophthalic acid with fuming nitric acid, until it no longer gives a precipitate with water.

*Potassium  $\gamma$ -mononitroisophthalate*,  $NO_2.C_6H_3(COOK)_2 + 1\frac{1}{2}H_2O$ , crystallises from aqueous alcohol in clusters of fine needles, and is very soluble in water. Heated at  $100^\circ$ , it loses  $\frac{1}{2}$  mol.  $H_2O$ , becoming slightly yellow; at higher temperatures, it smoulders to a black carbonaceous mass, swelling up and increasing in volume, like mercury sulphocyanate under similar circumstances; when heated quickly, it decomposes with slight explosion. It gives no precipitate with magnesium sulphate, mercuric chloride, manganese sulphate, cobalt nitrate, or nickel nitrate; but gives a precipitate on warming with calcium chloride, strontium nitrate, and with zinc and cadmium sulphates in the cold a white precipitate, soluble on heating; ferric chloride forms a brown-red precipitate; copper sulphate, a blue gelatinous precipitate; silver nitrate, a white crystalline precipitate, somewhat soluble on heating; lead acetate and mercurous nitrate, white precipitates. It is soluble in hot water (1.23 parts of water at  $99^\circ$  dissolves 1 part of the substance); on cooling the saturated solution, it solidifies to a hard mass. It loses its water of crystallisation on heating.

*Sodium  $\gamma$ -mononitroisophthalate* is obtained pure in short needles by precipitating a saturated aqueous solution with alcohol; the potassium salt may also be purified in this manner. Heated to  $160^\circ$ , it turns reddish-yellow, and detonates at higher temperatures.

*Ammonium  $\gamma$ -nitroisophthalate* crystallises from water in brilliant leaflets. On evaporating its solution on a water-bath or on drying over sulphuric acid, it loses ammonia, and is converted into the acid salt,  $NO_2.C_6H_3(COO.NH_4).COOH$ .

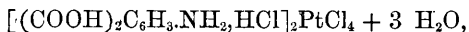
*Magnesium  $\gamma$ -mononitroisophthalate*,  $NO_2.C_6H_3:(COO)_2Mg + 5H_2O$ , forms small brilliant colourless crystalline granules, which form a hard crust on the walls of the vessel; 46.5 parts of water at  $15^\circ$

dissolve 1 part of salt. It loses  $\frac{1}{2}$  mol.  $\text{H}_2\text{O}$  over sulphuric acid, and the rest at  $150^\circ$ . The *calcium* and *barium* salts have already been described by Fittig (*loc. cit.*). The former is soluble in 140 parts of water at  $15^\circ$ ; the latter in 117 parts; the reddish barium salt loses its water of crystallisation over sulphuric acid, becoming yellow. The *strontium* salt,  $\text{NO}_2\cdot\text{C}_6\text{H}_3\cdot(\text{COO})_2\text{Sr} + 4\frac{1}{2}\text{H}_2\text{O}$ , forms stellate aggregations of beautiful prisms; loses 1 mol.  $\text{H}_2\text{O}$  over sulphuric acid, and the rest at  $150^\circ$ . It is very sensitive to light, turning deep violet-red; at  $100^\circ$  it becomes yellow. It requires 212 parts of water at  $15^\circ$  to dissolve it. The *zinc* salt forms crystalline granules with 1 mol.  $\text{H}_2\text{O}$ , which is given off at  $160^\circ$ : it is soluble in 182 parts of water. The *cadmium* salt crystallises in tufts of slender colourless needles with 2 mols. of  $\text{H}_2\text{O}$ , of which  $1\frac{1}{2}$  mol. is given off at  $100^\circ$ , and the remainder at  $160^\circ$ : it is soluble in 133 parts of water; its hot concentrated solution solidifies on cooling to a thick stiff jelly. The *lead* salt is a white gelatinous precipitate, afterwards somewhat crystalline, insoluble in water, when precipitated from the potassium salt by lead acetate. It is a basic salt, = the neutral salt +  $\frac{1}{4}\text{PbO}$ . The *copper* salt is thrown down as a blue gelatinous precipitate, when copper sulphate is added to the potassium salt: it is insoluble in water. When heated, it turns green, and finally detonates. It is a basic salt. The *silver* salt is a feebly yellow voluminous precipitate, only slightly soluble in water. It is coloured brownish by light or by heating at  $100^\circ$ ; at higher temperatures it detonates violently. The *manganese* salt is obtained in short thick prisms which turn brown in the air; or by quick cooling of a very hot solution, in slender needles which gradually change into brilliant granular crystals containing 5 mols.  $\text{H}_2\text{O}$ , half of which goes off over sulphuric acid, and the other half at  $150^\circ$ : it is soluble in 41 parts of water at  $15^\circ$ . The *ferric* salt is a gelatinous pale-brown precipitate. The *cobalt* salt forms pale-red round crystalline nodules, containing  $4\frac{1}{2}$  mols.  $\text{H}_2\text{O}$ , which go off at  $160^\circ$ ; the salt turns blue-violet at higher temperatures: it is soluble in 46.3 parts of water at  $15^\circ$ . The *nickel* salt forms small round bluish-green nodules, which lose their  $4\frac{1}{2}$  mols.  $\text{H}_2\text{O}$  at  $160^\circ$ , and turn yellowish-green; 36.5 parts of water dissolve 1 part of the salt.

*Ethyl  $\gamma$ -mononitroisophthalate*, already described by Storrs and Fittig (*loc. cit.*), fuses at  $83.5^\circ$ ; in resolidifying, small crystalline nodules appear in different parts of the fused mass, and from these stellate crystals spread in all directions, more nodules appear and more crystals until solid; these phenomena are accompanied by decrepitation, crackling, and contraction.

*Methyl  $\gamma$ -mononitroisophthalate*,  $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{COOMe})$ , prepared in a similar way to the ethyl compound, forms slender glistening white needles melting at  $121.5^\circ$ , soluble in alcohol; when warmed, it has an odour like that of aniseed. With  $\gamma$ -mononitroisophthalic acid (compare Storrs and Fittig, *loc. cit.*), the following additional reactions have been tried:—On heating, it becomes yellow. It gives with zinc sulphate, cadmium sulphate, silver nitrate, lead acetate, and mercuric chloride, white precipitates; with ferric chloride, brown; and with copper sulphate, pale green. It is soluble in 108.2 parts of water at  $99^\circ$ , and crystallises from the solution with 2 mols.  $\text{HO}_2$ ,

which go off at  $140^{\circ}$ . The hydrochloride has been already described (*loc. cit.*). The *platinochloride*,



forms dark yellow very thin small leaflets and prisms, mostly united in stellate and radiating groups; on heating, it turns red-yellow.

*γ-Amidoisophthalic acid hydrobromide*,  $(\text{COOH})_2\text{C}_6\text{H}_3\cdot\text{NH}_2\cdot\text{HBr}$ , crystallises in tufts of colourless needles or prisms, very soluble in water; on cooling hot concentrated solutions, firstly a magma forms, and finally quite a hard mass. The *nitrate* crystallises in very beautiful colourless tables and leaflets, or, if the cooling is slow, in thick prisms with  $1\frac{1}{2}$  mol.  $\text{H}_2\text{O}$ . It is not very soluble in cold water.

*Potassium γ-monamidoisophthalate*,  $(\text{COOK})_2\text{C}_6\text{H}_3\cdot\text{NH}_2$ , is very soluble in water; it crystallises from 90 per cent. alcohol in slender needles. The *sodium salt* is analogous to the potassium salt. The *magnesium salt* crystallises in extremely slender long needles with  $4\frac{1}{2}$  mols.  $\text{H}_2\text{O}$ , which are given off at  $130^{\circ}$ . It dissolves in 5 parts of water at  $15^{\circ}$ ; the solution turns brown, but in a lesser degree than the calcium and strontium salts. The *calcium salt* crystallises in globular aggregations and crusts of fine needles, with  $3\frac{1}{2}$  mols.  $\text{H}_2\text{O}$ , given off at  $150^{\circ}$ ; soluble in 13.4 parts of water at  $15^{\circ}$ . The *strontium salt* forms small tables and leaflets, with 1 mol.  $\text{H}_2\text{O}$ , which it loses at  $150^{\circ}$ , and changes to brilliant scales: it is soluble in 11.61 parts of water at  $15^{\circ}$ . The *barium salt* forms brown-red radiating prisms, with  $1\frac{1}{2}$  mol.  $\text{H}_2\text{O}$ , which is given off at  $150^{\circ}$ : it is soluble in 18.42 parts of water at  $15^{\circ}$ . The *zinc salt* is an insoluble crystalline precipitate. The *cadmium* and *lead salts* are amorphous insoluble precipitates. The *silver salt*,  $\text{COOH}(\text{COOAg})\text{C}_6\text{H}_3\cdot\text{NH}_2$ , is precipitated from the neutral potassium salt by silver nitrate; it forms microscopic prisms. By boiling with water, it is completely decomposed with the deposition of silver.

*Ethyl γ-monamidoisophthalate*,  $(\text{COOEt})_2\text{C}_6\text{H}_3\cdot\text{NH}_2$ , made by reducing the nitroisophthalate. Zinc-dust is gradually added to a mixture of 50 grams ethyl nitroisophthalate, 300 grams absolute alcohol, and 500 grams strong hydrochloric acid, cooled with ice. The product is poured into water, and the insoluble ethyl salt filtered off, and crystallised from alcohol. It forms tufts of colourless thin leaflets (m. p.  $118^{\circ}$ , resolidifies about  $113^{\circ}$ ), very slightly soluble in water, from which it crystallises in long slender needles, very soluble in ether. The solutions show a violet fluorescence.

*Methyl γ-monamidoisophthalate*,  $(\text{COOMe})_2\text{C}_6\text{H}_3\cdot\text{NH}_2$ , prepared from the nitroisophthalate in a similar manner to the ethyl compound; the amido-ether is separated by adding soda and sodium acetate to the solution; the white flocks are filtered off, washed, and crystallised from methyl alcohol; it then forms very thin broad, somewhat yellow, tables and leaflets, which glisten when dry. It is slightly soluble in water, and crystallises from the solution in tufts of long needles; it is very soluble in ether; the solutions are fluorescent. It melts at  $176^{\circ}$ , and resolidifies at about  $164^{\circ}$ . Like the ethyl compound, it becomes electric on warming.

If a sufficient quantity of potassium nitrite is gradually added to a very cold solution of *γ-amidoisophthalic acid hydrochloride*,



$\gamma$ -diazoisophthalic acid separates after some time as a reddish crystalline mass. When boiled with much water, it is converted into  $\gamma$ -hydroxyisophthalic acid, identical with that of Heine (Abstr., 1880, 549), and of Tönnies (Abstr., 1881, 50): by boiling with strong hydrochloric acid, a mixture of two acids is obtained, which, when neutralised with calcium carbonate and digested with lime, deposits hydroxyisophthalic acid as basic calcium salt, whilst the calcium salt of  $\gamma$ -monochlorisophthalic acid remains in solution. This acid,  $C_6H_3Cl(COOH)_2 + \frac{1}{2}H_2O$ , crystallises from water in long slender needles, generally in tufts (m. p.  $278^\circ$ ). The air-dried substance glistens, after drying at a high temperature; it is scarcely soluble even in hot water. It loses its  $\frac{1}{2}$  mol.  $H_2O$  at  $120^\circ$ : 1 part of acid dissolves in 3450 parts of water at  $15^\circ$ . It shows the following reactions:—With cadmium sulphate, an extremely bulky white precipitate, soluble when hot; with ferric chloride, a thick light-brown precipitate; with lead acetate, a thick white precipitate; with silver nitrate, similar, but soluble when hot; mercurous nitrate, a gelatinous white precipitate.

Potassium  $\gamma$ -monochlorisophthalate,  $C_6H_3Cl(COOK)_2$ , crystallises from water or alcohol in fern-like tufts of small needles. The sodium salt is similar to the potassium salt. The magnesium salt crystallises in hard rectangular tablets with 7 mols.  $H_2O$ , which are driven off at  $150^\circ$ : when its solution is cooled quickly, it is deposited in bunches of long slender needles, which ultimately turn into tablets. The calcium salt forms globular aggregations of small prisms, containing 2 mols.  $H_2O$ , driven off at  $140^\circ$ ; 1 part of this salt dissolves in 28.2 parts of water at  $15^\circ$ . The strontium salt crystallises in clusters of long hair-like needles, with 1 mol.  $H_2O$ , given off at  $140^\circ$ ; it is soluble in 108 parts of water at  $15^\circ$ . The barium salt is very similar to the strontium salt, has 2 mols.  $H_2O$ , given off at  $130^\circ$ , and is soluble in 71 parts of water at  $15^\circ$ . The cadmium salt forms nodular aggregations of very small needles, and is soluble in 330 parts of water at  $15^\circ$ . The copper salt is a crystalline blue precipitate, insoluble in water, and turns green when warmed. The silver salt,  $C_6H_3Cl(COOAg)_2$ , when first precipitated, is gelatinous, becomes gradually flocculent, and finally crystalline; it is soluble in hot water, and crystallises out in tufts of very small needles.

Ethyl  $\gamma$ -monochlorisophthalate,  $C_6H_3Cl(COOEt)_2$ , is prepared in the ordinary way by passing hydrochloric acid gas into an alcoholic solution of chlorisophthalic acid. It is precipitated in cold water, washed with soda, and then with water, and crystallised from alcohol. It forms short prisms melting at about  $45^\circ$ .  
D. A. L.

### Carbamic and Thiocarbamic Derivatives of Phthalic Acid.

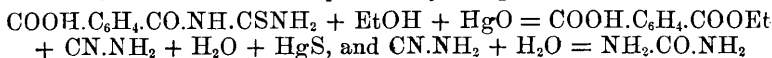
By A. PIATTI (*Gazzetta*, 12, 169—180).—When phthalic anhydride is heated with urea at temperatures above  $130^\circ$ , phthalimide (m. p.  $229^\circ$ ) is formed with evolution of ammonia and carbonic anhydride; but below that temperature the reaction is different. An intimate mixture of phthalic anhydride and urea, when heated, begins to melt at  $118^\circ$ ; the temperature is then gradually raised to  $125^\circ$ , and as soon as carbonic anhydride begins to be evolved the lamp is removed. The residue is then exhausted with cold water, which dissolves the ammonium

phthalate formed, washed with ether, and crystallised from boiling water. The *phthalocarbamic acid*,  $\text{COOH.C}_6\text{H}_4\text{.CO.NH.CONH}_2$ , thus obtained, crystallises in stellate clusters of lustrous scales, almost insoluble in ether and in cold water, but dissolving in 28.9 parts of water at  $99^\circ$ . It does not melt, but begins to decompose above  $150^\circ$ , leaving a residue of phthalimide, but no ureide is formed. The barium, sodium, and silver salts are described; they are all crystalline.

*Phthalic ureide*,  $\text{C}_6\text{H}_4\text{: (CONH)}_2\text{: CO}$ , is not formed by the action of phthalic anhydride or chloride on urea, but may easily be obtained by treating phthalocarbamic acid with phosphorus oxychloride; the product is mixed with ether, and the precipitate, after being washed with ether, is crystallised from boiling water or alcohol. It forms long silky needles, which decompose at  $185\text{--}190^\circ$  without evolution of gas, yielding phthalimide and cyanuric acid. *Silver phthalic ureide* crystallises in long slender needles.

*Phthalothiocarbamic acid*,  $\text{COOH.C}_6\text{H}_4\text{.CO.NH.CSNH}_2$ .—This is obtained in a manner similar to the carbamic acid by heating thiocarbamide with phthalic anhydride at about  $130^\circ$ ; the mass softens, melts, and again solidifies without any gas being evolved. Purified in the manner above described, the new acid crystallises in long needles or large plates, almost insoluble in ether and benzene. It melts at  $171\text{--}172^\circ$  with decomposition, phthalimide, ammonia, and carbon oxysulphide being produced. The *barium salt* crystallises in colourless needles of the formula  $(\text{C}_6\text{H}_4\text{N}_2\text{O}_3\text{S})_2\text{Ba} + 7\text{H}_2\text{O}$ .

When phthalothiocarbamic acid in alcoholic solution is treated with mercuric oxide, it yields monethyl phthalate,  $\text{COOH.C}_6\text{H}_4\text{.COOEt}$ , and urea, the reactions in all probability being—

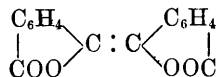


The acid, when heated with anhydrous alcohol and copper at  $120\text{--}130^\circ$ , gives monethyl phthalate and thiocarbamide.

C. E. G.

**Diphthalyl.** By C. GRAEBE and H. SCHMALZIGANG (*Ber.*, **15**, 1673 1675).—The vapour-density of diphthalyl (m. p.  $334^\circ$ ) was found to be 8.97, corresponding with the formula  $\text{C}_{16}\text{H}_8\text{O}_4$ . At the ordinary temperature, bromine unites with diphthalyl, forming an addition-product,  $\text{C}_{16}\text{H}_8\text{O}_4\text{Br}_2$ , crystallising in microscopic plates, soluble in chloroform. This compound begins to soften at  $220^\circ$ , and decomposes with evolution of bromine. The chief product of the action of a boiling solution of potash on the addition-product is diphtalic acid.

From these facts, the authors are inclined to regard the constitution of diphthalyl as—



An acid having the composition  $\text{C}_{16}\text{H}_{12}\text{O}_4$  is formed by the action of zinc-dust on an ammoniacal solution of diphthalyl.

W. C. W.

**Diphenylfumaric and Diphenylmaleic Acids.** By L. RÜGHEIMER (*Ber.*, **15**, 1625—1629).—The acid which Reimer (*Ber.*, **13**,

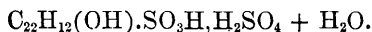
742; 14, 1797, and Abstr., 1881, 47; 1882, 169) obtained from dicyanostilbene, and to which he gave the name of diphenylfumaric or stilbenedicarboxylic acid, is a derivative of maleic acid, and should therefore be called *diphenylmaleic acid*. It can be prepared by the action of sodium on ethyl phenylbromacetate, diluted with three times its volume of anhydrous ether. When the evolution of hydrogen ceases, the liquid is decanted, and the residue washed with ether. After the ether has been removed by distillation, the residue is saponified with concentrated potash at 100°, and sufficient water is added to bring the potassium salt into solution: the liquid is then boiled with animal charcoal, and acidified with hydrochloric acid. The precipitate thus formed, after purification by recrystallisation from alcohol, yields pale yellow needles of the anhydride of diphenylmaleic acid,  $\text{Ph}_2\text{C}_2(\text{CO})_2\text{O}$ , melting at 155°. On adding water to the alcoholic mother-liquors, white crystals of diphenylfumaric acid,  $\text{Ph}_2\text{C}_2(\text{COOH})_2$ , are deposited: they are purified by treatment with boiling benzene and recrystallisation from glacial acetic acid. This acid melts at about 260°, splitting up into water and Reimer's stilbenedicarboxylic anhydride.

W. C. W.

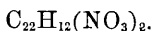
**Postscript to the Article on Tetraphenylthiocarbamide by Bernthsen and Fries** (*Ber.*, 15, 150). By A. BERNTHSEN (*Ber.*, 15, 1652).

**Ether of the Glycol  $\text{C}_{22}\text{H}_{14}\text{O}_2$ .** By G. ROUSSEAU (*Compt. rend.*, 95, 232—235).—The glycol  $\text{C}_{22}\text{H}_{12}(\text{OH})_2$ , obtained by the action of chloroform on  $\beta$ -naphthol (this vol., p. 1211), yields a series of ethereal salts when heated with acids. Concentrated boiling hydrobromic acid dissolves the glycol, and on cooling metallic green needles of the composition  $\text{C}_{22}\text{H}_{12}\text{Br}(\text{OH})\cdot\text{HBr} + 3\text{H}_2\text{O}$  separate out. These crystals dissolve in hot glacial acetic acid, which removes the hydrobromic acid and water, and on cooling, bronze-green needles of the composition  $\text{C}_{22}\text{H}_{12}(\text{OH})\text{Br} + \text{AcHO}$  are deposited. Hydrochloric acid, heated with the glycol at 160° for several hours, yields a similar compound, which behaves in the same way with acetic acid. Hydriodic acid removes one of the hydroxyl-groups, and yields a saturated compound of the composition  $\text{C}_{22}\text{H}_{12}\text{I}_2(\text{OH})\text{I}$ : the same derivative is formed by the action of hydriodic acid at 160° on the true ether of the glycol,  $\text{C}_{22}\text{H}_{12}\text{O}$ . It is a greenish-brown powder, which does not decompose below 100°, and is but slightly soluble in most solvents. The corresponding bromine-compound is obtained by treating the glycol with a solution of bromine in carbon bisulphide. The bromine-compound is also obtained by the action of bromine on an acetic acid solution of the hydrobromic ether previously described. Hell and Ulrich have shown that only tertiary alcohols yield hydrobromic ethers with a solution of bromine in carbon bisulphide; it would appear therefore that  $\text{C}_{22}\text{H}_{12}(\text{OH})_2$  is an unsaturated tertiary glycol.

With sulphuric acid, the glycol yields an ethereal salt which dissolves in the acid diluted with half its volume of water, and crystallises from this solution in reddish-brown plates of the composition—



Nitric acid yields a resin which appears to be the ethereal mononitrate, together with red needles (m. p. 190°) of the composition—



The diacetate,  $\text{C}_{22}\text{H}_{12}(\text{OAc})_2$ , has been previously described.

All these salts, with the exception of the diacetate and hydriodide, when dissolved in boiling alcohol, yield deep red solutions, but after some minutes' ebullition the colour rapidly disappears, and a crystalline magma of the true ether,  $\text{C}_{22}\text{H}_{12}\text{O}$ , separates out. It is evident that this ether is highly stable, and that all the derivatives of the glycol have a tendency to be converted into it. It may be formed (1) by the action of dehydrating agents on the glycol; (2) by the regulated action of reducing agents on the ethereal salts; (3) and in small quantities by the action of chloroform on  $\beta$ -naphthol.

When treated with alcoholic potash, the ethereal salts of the glycol are converted into the ethylic ether,  $\text{C}_{22}\text{H}_{12}(\text{OH})\text{OEt}$ , m. p. 144°.

C. H. B.

**Angelica Oils.** By F. BEILSTEIN and E. WIEGAND (*Ber.*, **15**, 1741—1742).—The oil extracted from the roots of *Angelica archangelica* consists almost entirely of terpenes,  $\text{C}_{10}\text{H}_{16}$ , boiling at 158° (sp. gr. 0.8609 at 16.5°), at 176° (sp. gr. 0.8481 at 16.5°), and a third portion which distils at 250°.

W. C. W.

**Oil of Cinnamon Leaves.** By E. SCHAEER (*Arch. Pharm.* [3], **20**, 492—498).—The author confirms most of Stenhouse's (*Pharm. J. Trans.*, **14**, 319; *Annalen*, **95**, 103) experiments on the oil of cinnamon leaves. The author found that the sp. gr. = 1.049 at 18.5° C. (1.053 Stenhouse). He could not detect benzoic acid, which Stenhouse found to be present, and he considers the oil to contain a body of the nature of an aldehyde, but in very small quantity.

F. L. T.

**Bromo-derivatives of Camphor.** By T. SWARTS (*Ber.*, **15**, 1621).—When monobromocamphor is treated with phosphorus pentabromide in an open vessel at a gentle heat,  $\alpha$ -dibromocamphor is produced. This compound has recently been described by Kachler and Spitzer. A totally different reaction takes place, however, at 110°, in closed tubes.

$\alpha$ -Dibromocamphor is not attacked by phosphorus pentabromide at 100°, but  $\beta$ -dibromocamphor is converted into the tribromo-derivative.

Phosphorus chlorobromide attacks camphor at the ordinary temperature, forming a crystalline body,  $\text{C}_{10}\text{H}_{14}\text{Br}_4$ , and other products.

W. C. W.

**Isomerism of Dibromocamphor.** By T. SWARTS (*Ber.*, **15**, 1662—1665).—When a mixture of bromine and monobromocamphor is exposed in sealed tubes to the action of the sunlight at the ordinary temperature for several months,  $\beta$ -dibromocamphor (m. p. 114.5°) is produced. If the sealed tubes are opened from time to time to permit the

hydrobromic acid which is evolved, to escape, the product consists of  $\alpha$ -dibromocamphor, melting at  $57^\circ$ . Attempts to convert  $\alpha$ -dibromocamphor into the  $\beta$ -modification, by the prolonged action of hydrobromic acid at  $120^\circ$ , were unsuccessful; when, however, the  $\alpha$ -derivative is heated with bromine at  $120^\circ$ , it is partly converted into the  $\beta$ -derivative. When  $\beta$ -dibromocamphor is boiled with bromine for 24 hours, it yields tribromocamphor,  $C_{10}H_{13}Br_3O$ , melting at  $64^\circ$ .  $\alpha$ -Dibromocamphor undergoes no change under similar treatment.

100 parts of absolute alcohol at  $20^\circ$  dissolve 22 parts of  $\alpha$ - and 3.75 parts of  $\beta$ -dibromocamphor. The  $\alpha$ -derivative is deposited from an alcoholic solution in crystals which resemble potassium nitrate in appearance;  $\beta$ -dibromocamphor crystallises in plates resembling silver nitrate.

W. C. W.

**Products of the Distillation of Colophony.** By A. RENARD (*Compt. rend.*, 245—247); see also this vol., 737 and 1179; and 40, 738).—The hydrocarbon *decine*,  $C_{10}H_{18}$ , previously described (this vol., 737), is really a mixture of olefines with small quantities of hydrocarbons of the benzene series. When the whole series of hydrocarbons boiling between  $90^\circ$  and  $160^\circ$  is treated repeatedly with sulphuric acid, then washed with soda and distilled, three fractions are obtained, boiling respectively at  $96^\circ$ ,  $120^\circ$ , and  $150^\circ$ .

The first fraction consists of an olefine,  $C_7H_{14}$ , mixed with small quantities of toluene, from which it may be separated by treatment with Nordhausen sulphuric acid. The purified hydrocarbon  $C_7H_{14}$  boils at  $95$ — $98^\circ$ ; sp. gr. at  $20^\circ = 0.742$ ; vapour-density, 3.48. It is soluble in alcohol and ether, and does not act on polarised light. Hydrochloric acid gas and nitric acid of sp. gr. 1.36, are without action, but fuming nitric acid attacks the hydrocarbon somewhat violently. In diffused daylight, the hydrocarbon dissolves bromine, but no addition-products are formed; in direct sunlight, however, the red colour disappears, and hydrobromic acid is given off.

The second fraction contains the hydrocarbon  $C_8H_{16}$ , mixed with xylene. The purified olefine boils at  $120$ — $123^\circ$ ; sp. gr. at  $19^\circ = 0.764$ ; vapour density, 3.97. Its properties are identical with those of its preceding homologue.

The third fraction contains the hydrocarbon  $C_9H_{18}$ , mixed with xylene and cumene. When purified this olefine boils at  $147$ — $150^\circ$ ; sp. gr. at  $20^\circ = 0.787$ ; vapour-density, 4.48. Its properties are identical with those of the olefines  $C_7H_{14}$  and  $C_8H_{16}$ .

C. H. B.

**Euxanthone.** By C. GRAEBE and R. EBRARD (*Ber.*, 15, 1675—1680).—Euxanthone melts at  $232^\circ$ . Its vapour-density is 7.96, corresponding with the formula  $C_{13}H_8O_4$ . When euxanthone is heated at  $100^\circ$  with methyl iodide, methyl alcohol, and potash in sealed tubes, *dimethyleuxanthone*,  $C_{13}H_8O_4Me_2$  is produced. On recrystallisation from chloroform, it is obtained in yellow needles or prisms (m. p.  $130^\circ$ ), freely soluble in ether, chloroform, and in hot alcohol. The *ethylic ether*,  $C_{13}H_8O_4Et_2$ , crystallises in colourless prisms (m. p.  $126^\circ$ ).

*Dibenzoyl euxanthone*,  $C_{13}H_8O_4Bz_2$ , prepared by heating a mixture of euxanthone with benzoic chloride at  $180^\circ$ , forms brown crystals

(m. p.  $214^{\circ}$ ), soluble in hot aniline, but insoluble in alcohol, ether, chloroform, benzene, and ethyl acetate.

The body obtained by Wichelhaus and Salzmann (*Ber.*, **10**, 1397; *Abstr.*, 1878, 79) by the reduction of euxanthone with zinc-dust, consists of the methylene diphenyl oxide of Merz and Weith (*Ber.*, **14**, 187), rendered impure by the presence of a hydrocarbon.

By the action of ammonia on euxanthone at  $180^{\circ}$ , a portion of the oxygen is replaced by nitrogen. W. C. W.

**Quassiin.** By A. CHRISTENSEN (*Arch. Pharm.* [3], **20**, 481—492). The literature of quassiin is comparatively unimportant, Winckler's (*Buchner's Repertorium*, **54** [1837], 85; and **65** [1839], 74) and Wiggers's (*Annalen*, **21** [1837], 40) being the only papers of any note.

The authors exhausted quassia with water, and precipitated the quassiin by tannin, after neutralisation with sodium carbonate. The tannate was mixed with lead carbonate (or calcium hydroxide), dried, and the quassiin was extracted by alcohol. The author found the amount of quassiin in the quassia to vary largely, some specimens yielding scarcely any. Pure quassiin, purified by recrystallisation from hot alcohol, crystallises in very thin rectangular plates, which are biaxial, and doubly refracting. It is bitter, odourless, permanent in the air, and its solutions are neutral. It melts at  $205^{\circ}$ , swelling up slightly to a resinous mass of unchanged quassiin. It is readily soluble in alkalis, and is reprecipitated by acids. It is soluble in boiling alcohol, less so in cold. Ether and light petroleum dissolve it with difficulty, chloroform very easily. It is dextrorotatory, its specific rotatory power for  $[\alpha]_D$  being  $+37.8$ . Its formula is  $C_{31}H_{42}O_9$  ( $C_{20}H_{25}O_6$ , Wiggers). It is precipitated by tannin. It is not a glucoside, but by the prolonged action in the water-bath of 3 per cent. sulphuric acid, a body,  $C_{31}H_{38}O_9$ , is formed, which dissolves sparingly in water, giving no precipitate with tannin; unlike quassiin, its aqueous or alcoholic solution reduces silver nitrate: a resin is simultaneously formed by the action of the dilute acid.

A bromo-derivative of quassiin (m. p.  $75^{\circ}$ ) was formed by the action of bromine in chloroform solution. Contrary to the statements of Bennerscheidt, the author found free fatty acids in quassia wood, but no essential oil. F. L. T.

**Pyridine Bases derived from Brucine.** By O. DE CONINCK (*Compt. rend.*, **95**, 298).—Brucine, when distilled with potash, yields oily products closely resembling the crude quinoline obtained in a similar manner from cinchonine. The fraction  $164\text{--}170^{\circ}$  contains a base, boiling at  $166^{\circ}$ , insoluble in water, and having all the properties of the  $\beta$ -lutidine obtained from cinchonine. The fraction  $175\text{--}185^{\circ}$  contains a collidine, boiling at  $180\text{--}182^{\circ}$ , in all probability identical with the  $\alpha$ -collidine obtained from cinchomine; and the fraction  $190\text{--}200^{\circ}$ , which is four times as large as the preceding fraction, contains a collidine boiling at  $196^{\circ}$ , and undoubtedly identical with the  $\beta$ -collidine contained in crude quinoline. It is evident that when cinchonine and brucine are distilled with potassium hydroxide, two isomeric series of pyridine bases are formed simultaneously. C. H. B.

**Action of Ethylene Chlorhydrin on Pyridine Bases and on Quinoline.** By A. WÜRTZ (*Compt. rend.*, **95**, 263—267).—Aldehydine (b. p. 179—182°), obtained by the distillation of aldol-ammonia, is mixed with an equal weight of water, and heated with ethylene chlorhydrin in molecular proportion in a sealed tube at 100° for several days. When the oily layer has disappeared, the liquid is exhausted with ether, to remove unaltered aldehydine and chlorhydrin, and the aqueous solution of the hydrochloride, concentrated by evaporation, is mixed with platinum chloride, and the platinumochloride is recrystallised several times from warm water. Thus purified, the *oxethyl-aldehydine platinumochloride*,  $(C_8H_{11}NCl.OEt)_2PtCl_4$ , forms large orange-red, apparently monoclinic crystals, somewhat soluble in warm water. The boiling concentrated solution becomes turbid on cooling, and deposits oily drops, which eventually crystallise. When heated at 100°, the platinumochloride loses hydrochloric acid; when decomposed by hydrogen sulphide, it yields a colourless hydrochloride, which will not crystallise. Treated with silver oxide and water, it yields a soluble caustic base, which absorbs carbonic anhydride from the air. This new base is analogous to the *neurine* obtained by the action of ethylene chlorhydrin on trimethylamine.

$\alpha$ -Collidine (b. p. 178—183°), obtained by the distillation of cinchonine with potash, when treated in a precisely similar manner, yields a much less soluble and much less stable orange-yellow platinumochloride, which is partially decomposed by hot water. If the aqueous solution is boiled for some minutes, then treated with hydrogen sulphide and concentrated, reddish-brown crystals are obtained, which when purified by crystallisation from alcohol, form brilliant brownish plates; these consist of *oxethyl- $\alpha$ -collidine platinosochloride*, derived from the *oxethyl- $\alpha$ -collidine platinumochloride*,  $(C_{10}H_{16}NOCl)_2PtCl_4$ , by loss of 2 molecules of hydrochloric acid. Oxethyl- $\alpha$ -collidine hydrochloride, obtained by the action of hydrogen sulphide on the unaltered platinumochloride, yields with gold chloride an abundant precipitate of deep yellow drops, which soon form crystals, easily fusible under hot water. These crystals dissolve in a large quantity of boiling water, and on cooling long slender golden-yellow needles of the aurochloride separate out.

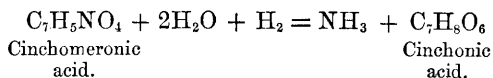
When quinoline (b. p. 238—240°), obtained by distilling cinchonine with potash, is heated with ethylene chlorhydrin and water, it yields *oxethyl-quinoline hydrochloride*,  $C_9H_7NCl.OEt$ , which when purified forms large colourless hygroscopic prisms, having a bitter taste, and very soluble in water or alcohol, but insoluble in ether. The aqueous solution gives no precipitate with ammonia, but an abundant coloured precipitate with potash. When boiled with silver oxide or lead hydroxide, it is decomposed with formation of a strongly alkaline solution. With mercuric chloride, the hydrochloride forms a compound which crystallises in brilliant colourless plates; the composition of these corresponds more closely with the formula  $5C_{11}H_{12}NOCl.6HgCl_2$  than with  $C_{11}H_{12}NOCl.HgCl_2$ . The aurochloride forms beautiful yellow crystals, soluble in boiling water, and the platinumochloride  $(C_{11}H_{12}NOCl)_2PtCl_4$  forms opaque indistinct orange crystals, soluble in a large quantity of boiling water.

When heated with ethylene chlorhydrin alone, quinoline forms a

deep violet mass, which, on being repeatedly treated with alcohol and ether, yields colourless crystals, apparently identical with the hydrochloride described above.

C. H. B.

**Cinchonic and Pyrocinchonic Acids.** By H. WEIDEL and R. BRIX (*Monatsh. Chem.*, **3**, 603—621).—The action of hydrogen on a solution of sodium cinchomerone gives rise to a non-azotised acid (cinchonic acid), the formation of which is attended with elimination of ammonia and assumption of water and hydrogen—



The cinchomeronic acid used in the authors' experiments was prepared, according to the method of Hoogewerff and van Dorp (*Ber.*, **14**, 974), by boiling pyridine-tricarboxylic acid with glacial acetic acid:  $\text{C}_5\text{H}_2\text{N}(\text{COOH})_3 = \text{C}_7\text{H}_5\text{NO}_4 + \text{CO}_2$ . To convert it into cinchonic acid, solid sodium amalgam is added to a boiling solution of 60 g. sodium cinchomerone in 25 litres of water, as long as ammonia continues to escape; the separated mercury is poured off; and the solution is mixed with sulphuric acid in such quantity as to convert about one-fourth of the soda into acid sulphate. On evaporating to dryness, exhausting the residue with absolute alcohol, and distilling off the alcohol, there remains a pale yellow syrup, still containing sulphuric acid and soda, the former of which may be removed by barium carbonate. The concentrated solution of barium cinchonate is then to be precipitated with basic lead acetate, and the precipitate decomposed by hydrogen sulphide, whereby a colourless solution is obtained, which on evaporation leaves the cinchonic acid in the form of a nearly colourless syrup, and this, after long standing over sulphuric acid, solidifies to a soft hygroscopic crystalline mass.

Cinchonic acid, in presence of traces of a mineral acid, changes gradually into a thick oily mass, which requires long boiling with water to revert it into the original acid. This alteration, also produced by prolonged heating, is probably due to the formation of an anhydride or lactone.

*Barium cinchonate*,  $\text{C}_7\text{H}_5\text{BaO}_6$ , is nearly insoluble in cold, moderately soluble in hot water, and crystallises with 4 mols.  $\text{H}_2\text{O}$ , which are not given off below  $200^\circ$ . With silver nitrate its solution gives a white pulverulent precipitate of the salt  $\text{C}_7\text{H}_5\text{Ag}_2\text{O}_6$ ; with lead acetate, normal or basic, a white precipitate, which when thrown down by basic lead acetate at the boiling heat, changes, like lead malate, into a greasy mass.

*Pyrocinchonic anhydride*,  $\text{C}_6\text{H}_6\text{O}_3$ , is formed, together with a small quantity of oily substance, by the dry distillation of cinchonic acid:  $\text{C}_7\text{H}_8\text{O}_6 = \text{C}_6\text{H}_6\text{O}_3 + \text{CO}_2 + \text{H}_2\text{O}$ . After repeated crystallisation from ether, it melts at  $94.2^\circ$ ; after sublimation, at  $95.1^\circ$ . From solution in benzene, ether, chloroform, or acetone, it separates in large nacreous rhombic laminæ or tablets, which are especially fine when crystallised from acetone. Axes,  $a:b:c = 0.6265:1:1.5208$ . Forms  $\infty P\infty$ ,  $\infty P\infty$ ,  $0P \cdot \infty P$ . Cleavage basal.



The metallic pyrocinchonates, obtained by boiling pyrocinchonic anhydride with the corresponding carbonates, are microcrystalline salts. The *calcium salt*,  $C_6H_6CaO_4$ , separates from its solution by spontaneous evaporation, in chalky microscopic crystalline splinters, and, like the normal butyrate and valerate of calcium, is precipitated from solution at the boiling heat. When submitted to dry distillation, all the pyrocinchonates yield, not the acid  $C_6H_6O_4$ , but the anhydride  $C_6H_6O_3$ .

*Pyrocinchonimide*,  $C_6H_6(NH)O_2$ , is obtained by heating pyrocinchonic anhydride in a sealed tube at  $100^\circ$ , for two hours, with a concentrated solution of ammonia in absolute alcohol,  $C_6H_6O_3 + NH_3 = H_2O + C_6H_7NO_2$ , and separates from solution in dilute alcohol in triclinic prisms.

*Hydropyrocinchonic acid*,  $C_6H_{10}O_4$ , isomeric with adipic acid, is formed by the action of sodium-amalgam on pyrocinchonic anhydride, according to the equation  $C_6H_6O_3 + H_2O + H_2 = C_6H_{10}O_4$ , and crystallises from water in dull white spherical geodes. It is moderately soluble in alcohol, and often separates therefrom in larger needles, having a vitreous lustre and belonging to the triclinic system. When heated, it sublimes in feathery crystals, and melts, after recrystallisation from water, at  $189^\circ$ , after sublimation at  $186.5^\circ$ . It appears at the same time to be partly converted into an anhydride, for the acid melted in capillary tubes does not solidify till after 24 hours, and then melts at  $151-153^\circ$ .

The analyses of the normal calcium and acid ammonium salt show that this acid is bibasic. The *calcium salt*,  $C_6H_6CaO_4$ , is but slightly soluble even in hot water, and separates from concentrated solutions in silky monoclinic needles, containing  $1\frac{1}{2}$  mols.  $H_2O$ , which they give off only at a very high temperature.—The *acid ammonium salt*,  $C_6H_9(NH_4)O_4$ , forms monoclinic prisms, having a vitreous lustre, and easily soluble in water, either warm or cold. Axes,  $a : b : c = 0.768 : 1 : 0.605$ . Angle  $ac = 107^\circ$ . Forms  $0P$ ,  $\frac{1}{2}P\infty$ ,  $\infty P$ ,  $\frac{1}{2}P\infty$ . Cleavage indistinct.

The conversion of pyrocinchonic anhydride into an acid,  $C_6H_{10}O_4$ , is likewise effected by the action of hydriodic acid and phosphorus, aided by heat. At the same time, however, a volatile acid is produced, the composition of which has not yet been made out.

Of the nine possible adipic acids,  $C_6H_{10}O_4$ , the following eight have been previously obtained :—

	M. p.		M. p.
Normal adipic acid ..	148—149°	Unsym. dimethylsuccinic acid .....	74°
$\alpha$ -Methyl-glutaric acid	76	Propylmalonic acid. .	96
Ethylsuccinic ..	98	Isopropylmalonic acid	87—91
Symmetrical dimethylsuccinic acid .....	165—167	Ethyl-methylmalonic acid .....	118

Lastly, Tate supposes that an acid,  $C_6H_{10}O_4$  (m. p.  $135-140^\circ$ ),  
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obtained by the oxidation of camphor, is the ninth member of the series, viz.,  $\beta$ -methylglutaric acid. Hydropyrocinchonic acid differs so greatly in melting point ( $189^\circ$ ) from any of these, that it cannot possibly be identified with either of them, supposing their melting points to have been correctly determined. It approaches, however, most nearly in melting point to normal adipic and symmetrical dimethylsuccinic acid, and in its mode of crystallisation and the characters of some of its salts, it does not differ greatly from normal adipic acid; but its identity with either of these acids cannot be positively determined without further experiments.

The conversion of cinchonic acid into pyrocinchonic anhydride is accompanied, as already observed, by the formation of an oily body; and on treating this substance with sodium-amalgam, there is obtained, together with the adipic acid melting at  $189^\circ$ , a small quantity of another compound, much more soluble in water, and separable from the pyrocinchonic anhydride by repeated crystallisation. This substance, obtained in small quantity only, sublimes easily in slender shining needles, and crystallises from aqueous solution in small apparently prismatic needles, melting at  $121^\circ$ . It is probably identical with ethylmethylmalonic acid (m. p.  $118^\circ$ ). It evidently owes its origin to the oily product abovementioned, and seems to indicate that this latter is produced by molecular transformation of cinchonic acid at the high temperature of the distillation.

By heating pyrocinchonic anhydride and bromine in molecular proportion at  $100^\circ$  in a sealed tube, dibromacetic acid,  $C_2H_2Br_2O_2$ , is formed, and may be obtained by agitating the product with ether and distilling off the solvent, as a light yellow syrup, having a pungent tear-exciting odour, and solidifying in a vacuum after some time to a deliquescent radio-crystalline mass. The formation of this body is accompanied by that of another crystalline brominated compound, which, however, has not yet been obtained in quantity sufficient for investigation.

H. W.

**Hydroquinidine.** By C. FORST and C. BÖHRINGER (*Ber.*, **15**, 1656—1659).—The authors point out that Hesse's *hydroconquinine* (*Ber.*, **15**, 855, this vol., 1113) is identical with the alkaloid *hydroquinidine*, which they obtained by the action of potassium permanganate on quinidine sulphate (*Ber.*, **14**, this vol., 74). The *hydrochloride*,  $C_{20}H_{26}N_2O_2 \cdot HCl$ , forms anhydrous prismatic plates, freely soluble in water. The solution is dextrorotatory. The *hydrobromide*, prepared by adding potassium bromide to a warm dilute solution of the hydrochloride, crystallises in anhydrous plates, sparingly soluble in cold water. The *hydriodide* resembles the hydrobromide. The acid salt,



obtained by adding potassium iodide to a warm solution of the acid sulphate, forms large four-sided crystals of an orange colour.

The *normal tartrate*,  $(C_{20}H_{26}N_2O_2)_2 \cdot C_4H_6O_6 + 2H_2O$ , crystallises in thick glistening prisms soluble in water. The *acid tartrate*,



forms thin needles, sparingly soluble in cold water. The *thiocyanate*

crystallises in flat anhydrous prisms, which are nearly insoluble in cold water. The *benzoate* and the *salicylate* are deposited from alcohol in anhydrous colourless plates. The *acid sulphate* crystallises in white, and the *acid thiocyanate* in pale yellow needles. The normal oxalate forms transparent prisms. Quinidine sulphate invariably contains small quantities of hydroquinidine. When hydroquinidine is treated with hydrochloric acid at  $150^{\circ}$ , it yields methyl chloride, and a new base.

W. C. W.

**Quitenidine.** By C. FORST and C. BÖHRINGER (*Ber.*, **15**, 1659—1661).—In the preparation of hydroquinidine by the action of potassium permanganate on quinidine, the solution from which the hydroquinidine has been precipitated by an alkali, contains quitenidine,  $C_{19}H_{22}N_2O_4$ . The alkaline liquid is neutralised with dilute sulphuric acid, and rapidly evaporated. The alkaloid is deposited in white crystals; a further yield of the alkaloid is obtained by evaporating the mother-liquor nearly to dryness, and exhausting the residue with alcohol. After recrystallising the crude product from a mixture of alcohol (1 part), and water (3 parts), the alkaloid is obtained in fragile plates containing 2 mols.  $H_2O$ . The crystals melt at  $240^{\circ}$ , and decompose at  $246^{\circ}$ . They are soluble in hot water, alkalis, and acids. The fluorescence of the sulphuric acid solution is destroyed by the addition of hydrochloric acid. With chlorine-water and a drop of ammonia, the aqueous solution gives a green coloration, which changes to dark-violet on the addition of potassium ferrocyanide. Silver nitrate, and tannic acid produce white precipitates. Phosphotungstic and phosphomolybdic acids yield pale-coloured precipitates, soluble in ammonia. The *sulphate*,  $C_{19}H_{22}N_2O_4 \cdot H_2SO_4 + 3H_2O$ , forms white prisms; the *platinochloride*,  $C_{19}H_{22}N_2O_4 \cdot H_2PtCl_6 + 3H_2O$ , crystallises in large needles of an orange colour.

W. C. W.

**Bases found in Putrefaction Products.** By M. NENCKI (*J. pr. Chem.* [2], **25**, 47—52).—This paper is a claim to priority of research in the direction named.

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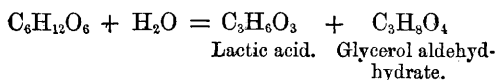
## Physiological Chemistry.

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**Physiological Oxidation.** By M. NENCKI and N. SIEBER (*J. pr. Chem.* [2], 25, 1—41).—The results of the investigations given in this paper are intended to supplement a previous series published in this Journal, and have for their object the determination of the part played by atmospheric oxygen in the decomposition of various organic bodies in alkaline solution at the body temperature. The substances chosen for experiment were such as exist and are liable to undergo these decompositions in the animal body.

In the previously recorded experiments, dextrose was found to

undergo lactic fermentation when digested in alkaline solution at the body temperature, certain bodies being formed, the special character of which was not accurately determined. The solutions were placed in flasks with rubber corks, and a stream of oxygen passed through them during the process of cooling; the flasks were then sealed and kept in an incubator at the body temperature for 48 hours, then opened and tested for dextrose, only traces being found. The lactic acid was determined by extraction with ether and conversion into the zinc salt; 47 per cent. of the dextrose was thus proved to have been converted into lactic acid. Experiments made to determine whether or not alkaline sugar-solutions absorbed oxygen gave affirmative results. The matter was then investigated quantitatively, and it was found in one case that the solution absorbed oxygen by weight to the extent of 14.55 per cent. of the sugar present, and in a second case 14.67 per cent. The carbonic anhydride produced was also determined, and found to be 2.32 per cent. and 2.23 per cent. by weight of the sugar used in the separate experiments, corrected for  $\text{CO}_2$  found in the alkali used; the  $\text{CO}_2$  was below 2 per cent. of the weight of sugar. The authors seek to explain this very small production of carbonic anhydride on the supposition that the sugar was chiefly broken up into lactic acid and glycerolaldehyd-hydrate—



Rénard describes under the name glycerolaldehyd, one of the bodies obtained by the action of electrolytic oxygen on glycerol, a white amorphous body of penetrating odour, slightly soluble in water, almost insoluble in alcohol (m. p. 71—72°). Such a body is not produced by the action of potassium hydroxide on dextrose when air is excluded. Henninger, however, considers the body to be impure trioxymethylene. The oxidation of dextrose in the presence of air, by which 50 per cent. of lactic acid is obtained, would thus find a simple explanation in the oxidation of the glycerolaldehyd to tartronic acid. The authors do not feel able to express an opinion on the matter from the results of their present experiments.

Elaborate experiments were next made with alkaline carbonates and dextrose, and it was again found that oxygen was absorbed. Experiments with very dilute solutions of dextrose, with both caustic and carbonated alkali, yielded the same result. Dilute watery solutions of dextrose were found not to absorb oxygen. Two bodies obtained from the solutions by extraction of the evaporated residue with ether, which reduced copper solutions and yielded crystallisable zinc salts; the quantities were, however, too small to admit of accurate investigation and analysis.

With these experiments as a basis, the authors investigated in the same way solutions of egg-albumin, peptone, and gluten, and found that oxygen was absorbed; special precautions were taken to exclude vegetable growths and prevent their formation. Gelatin solution, no absorption. Fibrin suspended in water showed no absorption, or at all events the amount was so small as to render it very doubtful.

Hufner's results are explained by the authors as due to the presence of fungoid growths. Serous fluids, serum of blood, solutions of leucine, tyrosine, glycocine, fatty acids, and neurine were investigated with varying results. Solutions of alkaline urates absorb oxygen, and the uric acid is converted into uroxic acid, and products of the further decomposition of the latter.

The authors sum up their results as follows:—

(1.) All the bodies experimented with absorbed more or less oxygen in alkaline solution, and the absorption depends—

( $\alpha$ .) On the molecular structure of the body.

( $\beta$ .) On the relative amount of alkali present, and the concentration of the solution.

( $\gamma$ .) On the duration of the action.

(2.) The amount of oxygen absorbed reaches a definite maximum which is not passed by allowing the action to continue.

(3.) Individual organic compounds, such as dextrose and albumin, were simultaneously decomposed by the alkali by hydration, but this hydration is not primary and necessary; the absorption of oxygen is not dependent upon it.

The remainder of the paper is devoted to criticism, and to the discussion of the results of administering citric acid in lactic acid in a case of diabetes.

W. N.

**Multiplication of Bacteria in the Blood of Living Animals by a Chemical Ferment Free from Organisms.** By ROSSBACH (*Bied. Centr.*, 1882, 569).—Papayotin introduced into the animal system caused the formation of innumerable globular and biscuit-shaped bacteria in the blood; thus, it would seem as if a chemical ferment was capable of increasing to a great extent the number of bacteria which are present only in small numbers under normal conditions.

E. W. P.

**Lactic Acid in the Urine in Disease, and Oxidation in the Tissues in Leukæmia.** By M. NENCKI and N. SIEBER (*J. pr. Chem.* [2], 25, 41—47).—The authors are of opinion that the presence of lactic acid in healthy urine, asserted by some investigators, requires further and more exact experiment for its proof. The paper contains an account of experiments on a leukæmic patient, and tends to show that the oxidations normally occurring in the body are enormously increased in this disease. Lactic acid was administered in large quantity, and none could be detected in the urine. 6 grams of benzene were given, and only 0.125 gram phenol was found in the urine.

W. N.

**Ewes' Milk as influenced by Fodder.** By H. WEISKE and G. KENNEDY (*Bied. Centr.*, 1882, 533—536).—A ewe was fed for 30 days with 0.5 kilo. hay, 0.5 kilo. barley, and 1 kilo. roots, and she was milked three times a day, when the milk became normal, which did not occur until 25 hours after lambing, while the colostrum was removed after the first half hour, then after 7 and 19 hours. The

percentages in the following table are calculated on 100 c.c. colostrum:—

Time elapsed since lambing.	Quantity, grams.	Specific gravity.	Dry matter, per cent.	Total proteids, per cent.	Casein, per cent.	Albumin, per cent.	Non-nitrogenous, per cent.	Fat, per cent.	Lactose, per cent.	Ash, per cent.
$\frac{1}{2}$ hour ...	64.6	1.0604	52.97	25.22	4.96	18.56	0.28	25.02	1.54	1.19
7 hours ...	170.0	1.0520	38.07	17.44	7.48	9.61	0.11	16.14	3.53	0.96
19 hours ..	288.0	1.0449	23.47	8.50	5.27	2.93	0.12	8.87	5.24	0.86
2 days ....	620.0	1.0359	17.21	5.22	4.28	0.82	0.11	5.93	5.19	0.87
4 " ....	768.0	1.0343	16.52	5.56	4.64	0.85	0.10	5.69	4.31	0.96
6 " ....	910.0	1.0335	14.78	4.88	3.88	0.70	0.08	4.47	4.55	0.88
8 " ....	992.0	1.0365	15.74	4.93	3.97	0.73	0.10	4.62	5.41	0.88
9 " ....	987.0	1.0358	15.61	4.59	4.49	0.60	0.08	4.74	5.41	0.90

The maximum yield occurred about the 9th day, and amounted to about 1000 cm., the dry matter rapidly fell in quantity up to the 5th day when it became regular. The same was the case with the sp. gr. With the allowance of food as above the weight and milk production remained constant. After 30 days, the ewe was shorn, and then the production of milk fell from 962 grams to 733 grams; but the addition of linseed cake brought the yield up to what it had been previously. Again the ewe was fed with 0.25 kilo. linseed cake and 0.5 barley, but the yield never rose above 1 litre, the average being 926 grams daily, and the composition was: dry matter, 161.8 grams. N  $\times$  6.25 50.4 grams. Fat, 62.0 grams. Lactose, 41.7 grams. Ash, 7.7 grams. Ewe's milk is therefore remarkable for its high percentage of dry matter, albuminoids, and fat.

E. W. P.

**Fossil Eggs in Guano.** By J. CLARK (*Bied. Centr.*, 1882, 567).—The following is the composition of fossil eggs of pelican and poto-yunco (*Puffinuna garnotii*) found in guano deposits on the island of Lobos at depths of 2—25 feet:—

	Pelican.		Potoyunco.
	White.	Black part.	White.
K <sub>2</sub> SO <sub>4</sub> .....	34·48	2·7	65·95
Na <sub>2</sub> SO <sub>4</sub> .....	10·45	0·95	17·98
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .....	8·70	1·58	10·70
Ammonium oxalate.....	31·07	4·95	—
NH <sub>4</sub> Cl .....	1·12	7·08	0·85
Am. phosph.....	2·24	5·86	1·74
Free acid .....	traces	traces	traces
Sol., organic.....	2·74	23·15	0·4
Insol., organic .....	0·93	43·50	0·83
(Sol. in ether) .....	—	(27·20)	—
Calc. phosph. ....	1·58	3·93	0·56
Silica .....	0·02	—	0·15
Water .....	6·70	6·30	0·84
<hr/>			
Nitrogen .....	100·00	100·00	100·00
	9·62	9·01	2·95

The centre of the pelican's egg was hard and black, whilst the outer part was yellowish-white, and the shell was black. The interior of the other egg was filled with pearly crystals.

E. W. P.



## Chemistry of Vegetable Physiology and Agriculture.

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**Fermentation of Starch: Presence of a Vibriole in Germinating Maize, and in the Stalk of the Plant.** By V. MARCANO (*Compt. rend.*, **95**, 345—346).—From time immemorial the American Indians have prepared a strongly alcoholic beverage, *chica*, by making a decoction of non-germinated maize and allowing it to ferment. The fermentation of this liquid is due to the reproduction of a highly characteristic organism which is deposited on the exterior pellicle of the grains of maize, and develops in three forms, vibrioles, nucleated globules similar to those of yeast, and mycelian tubes from which the vibrioles escape at certain times. By cultivation in suitable media, it is possible to observe the passage of one form into another. This ferment has the power of attacking young starch directly and rapidly, and also acts directly on full-grown starch, although more slowly. In both cases the products are dextrin, alcohol, and carbonic anhydride.

The organism resists the action of water boiling at 95° for several minutes, and develops most favourably between 40° and 45°, at which temperature it can produce the fermentation of mannitol. It also

ferments milk-sugar, saccharose, and glucose. During the fermentation of maize, the vibrios develop in the interior of the grain, and may be seen under the microscope in a state of incessant movement in the spaces between the starch granules. The vibrios are also present in the stalk of the maize plant, and are apparently localised in the tissues immediately under the bark. The presence of this organism on the exterior of a grain, its evident activity during the process of germination, and the connection of this process with true fermentation, will account for several hitherto unexplained facts, as for example the reabsorption of starch grains, which are not dissolved in their natural state by diastase.

C. H. B.

**Assimilation theoretically considered.** By J. REINKE (*Bied. Centr.*, 1882, 536—539).—Carbonic anhydride as it occurs in the plant-cells and chlorophyll grains must be in combination with water; such being the case, the question arises how is this compound,  $\text{H}_2\text{CO}_3$ , reduced so as to form carbohydrates, which must first appear in a soluble and diffusible condition?

The fermentation of glucose requiring six carbonic acid molecules necessitates the removal of 6 atoms of oxygen; but as carbonic acid does not possess the power of polymerising, the grouping of 6 C must be caused by some previous synthesis. The author then goes on to discuss the various ways in which  $\text{H}_2\text{CO}_3$  may be reduced, firstly, by the formation of formic acid; but the volumes of the oxygen thus eliminated would not correspond with the observed volumes, and also a further reduction of the formic acid is necessary before glucose is formed. Two atoms of oxygen may be lost with formation of formaldehyde which, when polymerised, would give glucose. In support of this view, attention is called to the presence of volatile reducing substances in the chlorophyll cells. Carbonic acid may lose all its oxygen, forming a hydrocarbon, probably ethylene, but this when oxidised would yield a fatty acid; whereas if methylene were formed and immediately oxidised, we should have formaldehyde. The author finally states his opinion, that carbohydrates are formed by removal of two atoms of oxygen from carbonic acid and consequent formation of formaldehyde; he founds his opinion on the fact that the volume of the gaseous mixture in which plants are growing remains absolutely constant.

E. W. P.

**Investigations as to the Quantity of Water necessary for Cereals.** By P. SORAUER (*Bied. Centr.*, 1882, 546—552).—From experiments on the growth of wheat, rye, barley, and oats in solutions of various concentrations, it would seem that, of the four cereals, oats are the least able to flourish in concentrated solutions, the strength of the solutions being 0.5, 2.5, 5.0, and 10.0 per cent. This is in accordance with the known facts that a crop of oats on a soil in poor condition is frequently better than that grown on the same soil which has been much improved by manuring. Each species and variety of plant requires a definite strength of solution to produce the maximum yield, for when the solution of plant food in the soil is too weak a large quantity must be absorbed to allow of complete nourishment; on the

other hand, if the solution is too strong, the plants do not increase much in size, but are much richer in ash. As wheat and rye flourish with strong solutions, these two crops may precede barley or oats, which do better on land which is not too rich in soluble matter; barley and oats will therefore flourish in soils which would starve wheat and rye. Plants growing in the more concentrated solutions deposit more dry matter in their roots than such as grow in the more dilute solutions, and the most favourable strength for the root-growth of all the cereals is, for wheat and rye 2·5 per cent. (with small addition of nitrogen), and 2·5 per cent. for barley and oats. Concerning the portion of the plants growing above ground, it appears that these portions are shorter the more concentrated is the solution of food material. As before stated, 2·5 per cent. appears to be the most advantageous strength for the growth of cereals, and in the case of wheat and rye with an additional quantity of 5 per cent. calcium nitrate; from such solutions they are enabled to deposit the maximum of dry matter with the minimum amount of absorption of water. The quantities of dry matter formed in the plants under observation were: rye, 235·5 grams; barley, 431 grams; wheat, 459, and oats 569 grams. These experiments offer an explanation of much that has been inexplicable in practical agriculture; the stronger solutions may be compared to a heavy soil which has been well worked and manured, whilst the dilute solutions resemble a poor, light sandy soil. Plants growing on the soils which have been heavily manured, and are therefore rich in soluble material, are smaller, feebler, slower growing, and richer in ash than if they had grown upon less rich soils; the roots remain short, and do not cover much ground; heavy manuring on such soils is therefore a loss, as is also deep ploughing; on the other hand, in more open and poorer soils the roots extend themselves further, absorbing a much greater quantity of water so as to provide food for the plant; if then there is a sufficiency of food in the soil, the yield will be satisfactory, and this is why light sandy soils are remunerative in wet seasons, and why some plants flourish only on certain soils.

E. W. P

**Ash of Cereals.** By E. R. MORITZ and A. HARTLEY (*Bied. Centr.*, 1882, 573).

	Water.	Ash.	In the Ash.			
			P <sub>2</sub> O <sub>5</sub> .	MgO.	CaO.	K <sub>2</sub> O.
Barley ....	13·7	2·76	25·3—38·8	2·9—11	1·2—4·2	19·8—37·2
Rice .....	14·04	2·34	60·2	4·25	7·2	20·2
Maize ....	14·26	1·02	53·7	18·6	0·6	28·4
Oats.....	16·89	3·92	14·5—29·2	5·9—8·2	1·38—8·35	13·1—24·3

E. W. P.

**Percentage of Potassium Carbonate and Phosphoric Acid in Wood Ashes.** By NESSLER (*Bied. Centr.*, 1882, 490).

	Beech.		Oak.	Scotch fir.		Pine.		Fir bark.
	Sticks.	Logs.		Sticks.	Logs.	Wood.	Bark.	
Pot. carbonate...	16.4	15.1	8.4	15.1	17.0	8.6	2.0	3.4
Phosphoric acid..	7.5	11.6	3.4	6.2	6.0	7.6	8.4	2.2

E. W. P.

**Experiments at Grignon in 1881.** By P. P. DÉHÉRAIN (*Bied. Centr.*, 1882, 445—452).—The crops of sainfoin were smaller than those obtained in 1880. It does not appear that the influence of sulphuric acid is harmless, and the potassium sulphate plots have borne a smaller crop than the unmanured plots. Peat was not of advantage. It is better to plough in farmyard manure than to top-dress with it, or with nitre or ammonium sulphate, as its after-action is more certain. On the plots which in 1881 bore wheat, and had in the previous five years grown potatoes variously manured, the best yield was obtained from those which had been heavily manured with farmyard manure. Peat and potassium sulphate produced no after-action. The best yield was from farmyard manure ploughed in during the previous year. Those roots which received no manure in 1881, but farmyard manure in 1880, were the largest crops except those treated with farmyard manure in 1880 and nitre in 1881. The best manure for oats was found to be farmyard and nitre. The powerful influence of potassium sulphate on maize was probably due to the abundance of humus, and this view is supported by the results obtained from peat and potassium sulphate. The after-action of nitre was small.

E. W. P.

**Cultivation without Animal Manures.** By SCHINDLER (*Bied. Centr.*, 1882, 568).—In Eschershausen, a farm whose soil is rich in alkalis has for 20 years past been manured only with artificials. The crops have always been good, and only a falling off in straw has been noticed when “silica” plants have been grown for 4—5 years consecutively, but the original yield has been obtained if a “lime” plant has been introduced into the rotation.

E. W. P.

**Influence of Superphosphates on the Percentage of Sugar in Beet.** By F. JACQUEMART (*Bied. Centr.*, 1882, 566).—According to Pellet, every 100 parts of sugar in the roots are accompanied by 1 part  $P_2O_5$ ; hence the author concludes that superphosphate must be applied in quantities proportional to the expected yield; 50,000 kilos. roots producing 6000 kilos. sugar per hectare requiring 528 kilos. of 12 per. cent. superphosphate.

E. W. P.

**Manuring of Sugar-beet.** By V. THIESSEN (*Bied. Centr.*, 1882, 520).—To compare the values of Chili saltpetre and Mejillones guano as manure for sugar-beet on marshy lands, plots were chosen which had borne barley or potatoes during the previous season.

Mejillones guano had no effect on the quantity, but the quality was greatly improved; on the other hand, Chili saltpetre, although somewhat lowering the quality, so raised the yield that this manure was by far the more profitable of the two. A mixture of the two manures raised the yield considerably, but the quotient of purity was greatly lowered.

E. W. P.

**Composition of Soil deposited by the Water employed for Washing Sugar-beet.** (*Bied. Centr.*, 1882, 568.)—The mud left in the washing vessels is by no means so valuable as is generally supposed, but still it is good enough to be put back on the land, or if the fields are distant, it may be mixed with liquid manure, blood, &c.

E. W. P.

**Value and Composition of Sheep-dung.** By E. LECOUTEUX (*Bied. Centr.*, 1882, 564).—The cost of preparation of the above manure was at the rate of 18·72 francs per 1000 kilos., but the value of the manure, giving the various constituents their market value, was 21·34 francs. The difference in favour of the natural product shows it to be a cheaper manure than the ordinary artificials. The composition of the sheep's dung as compared with that of oxen was as follows:—

	Sheep.	Oxen.
Water.....	71·00	83·61
Nitrogen .....	0·65	0·20
Phosphoric acid.....	0·16	0·11
Potash .....	0·59	0·27

E. W. P.

**Composition of Superphosphates.** By P. DE GASPARIN (*Bied. Centr.*, 1882, 565).—Superphosphates produce a great effect on the meadow lands of south-eastern France, even when 40 per cent of calcium carbonate is present in the soil. The crude phosphates—those employed in the manufacture of the soluble phosphate—contain as much as 42·8 per cent. of ferric oxide, but some organic matter is used in their preparation, which shows itself by an odour resembling acetic acid when the superphosphates are dried, and the analyses show that of the 12 parts of phosphoric acid present 10 parts exist as the free acid; lime and iron are as sulphates, and part of the sulphuric acid is free: when the phosphate is treated with alcohol, the iron is brought into solution by means of the above-mentioned organic matter.

E. W. P.

**Manuring Experiments with Soluble and Insoluble Phosphates.** By A. VÖLCKER (*Bied. Centr.*, 1882, 521—525).—The experimental field at Woburn was manured with various forms of phosphates and farmyard manure in various quantities. The results with turnips showed that finely ground coprolites and Redonda phosphate considerably raised the yield above that of the unmanured plot, and the yield with soluble phosphates was still higher. Heavy applications of farmyard manure were not more successful than half the quantity with crude or soluble phosphates in addition; the best re-

sults were obtained by the use of superphosphate and guano. In 1881 barley and red clover were sown on the same plots without additional manure, and we find that there was no remarkable difference between any of the plots. The best yield was from the heavy dressing of dung; and soluble phosphates gave better results in this second season than crude phosphates. E. W. P.

**Phosphoric Acid in Peruvian Guano.** By W. AVERDAM (*Bied. Centr.*, 1882, 566).—Ammonia is not present in guano in a volatile form, and the greater part of the phosphoric acid is present as mono- and bi-basic salts of magnesia, lime, and the alkalis. The action of sulphuric acid on guano is merely to remove chlorine, and causes the loss of 1 per cent. N present in an oxidised condition, and it also destroys valuable organic matter. E. W. P.

**Gypsum Manures.** By J. KÖNIG (*Bied. Centr.*, 1882, 567).—Gypsum residues from superphosphate factories contain about 2 per cent.  $P_2O_5$  and 50 per cent.  $CaSO_4$ , and residues from potash factories also contain 30 per cent. gypsum, as well as free lime, calcium carbonate, and 4—5 per cent. potash; but it sometimes happens that 22 per cent. calcium sulphite and thiosulphate is present, which renders these residues useless as manures. E. W. P.

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## Analytical Chemistry.

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**Conversion of Organic Nitrogen into Ammonia.** By H. GROUVEN (*Bied. Centr.*, 1882, 568).—According to this patent, steam heated to 400—700° is passed over the heated nitrogenous organic substance. The nitrogen is partially converted into ammonium carbonate, partially into higher nitrogenous compounds, but no nitrogen is set free. The vapour is then passed over a layer of Grouven's "contact mass," which completes the transformation into ammonia, and destroys all hydrocarbons, so that the issuing gas may be absorbed by acid without the production of a coloured liquid. This method may be used for nitrogen determination by using a porcelain boat in an iron tube to contain the substance. E. W. P.

**Detection of Chloride of Lime in Water.** By A. A. NESBIT (*Chem. News*, 46, 43).—The test solution is prepared by dissolving 100 grains of potassium iodide in 16 ounces of boiling water; 100 grains of starch in 1 ounce of cold water are gradually added, and the whole is boiled for 30 minutes. This solution is added in decreasing quantities to the water, beginning with 5 c.c.; the final quantity added, if the previous portions have shown no reaction, being 0.1 c.c., as it is found that the smaller the quantity of chlorine present the smaller is the quantity of test required to exhibit it. By this means  $\frac{1}{800}$  grain "available

chlorine" can be detected in a gallon. This process is intended for the examination of streams polluted by paper mills. E. W. P.

**Decomposition of Nitrous and Nitric Oxides by Heat.** By A. WAGNER (*Zeits. Anal. Chem.*, **21**, 374—380).—The estimation of nitrous oxide in mixtures of gases presents great difficulties, but the author has worked out a method which answers this purpose: it consists in passing the gaseous mixture, which must be quite free from oxygen, through a combustion tube containing a mixture of pure chromic oxide and sodium carbonate heated to redness. 1 c.c. of  $N_2O$  oxidises 2.283 mgrm. of chromic oxide to chromic acid, the amount of which is afterwards estimated, preferably by Rose's method.

Pure nitric oxide is not decomposed by chromic oxide, but when mixed with nitrous oxide, equal volumes of the gases are decomposed,  $N_2O + NO = NO_2 + 2N = 3N + 2O$ . O. H.

**New and Expeditious Method for the Determination of Nitrites under various Circumstances.** By E. W. DAVY (*Chem. News*, **46**, 1).—By this process, based on the oxidation of gallic acid by nitrous acid, small quantities of nitrites may be estimated, the presence of nitrates not interfering. A mixture of 25 c.c. of the water to be examined and 1—2 c.c. of gallic acid solution is heated in a test-tube with a few drops of hydrochloric or sulphuric acid, and when the coloured liquid has cooled it is compared with the colour produced by a mixture of standard acid and nitrite solutions under like conditions. The presence of organic matter and salts has no effect on the colour. If iron be present, it must be separated by ammonia before the addition of gallic acid. The gallic acid solution is a saturated one, rendered colourless by charcoal; the addition of sulphuric or hydrochloric acid prevents the change of colour which may take place after keeping. The standard alkaline nitrite solution is prepared by decomposing silver nitrite by sodium chloride: 0.406 gram of the silver nitrite is decomposed, and the solution made up to 1 litre, and of this when clear 100 c.c. is diluted to 1000 c.c., of which 1 c.c. is equivalent to 0.01 gram  $N_2O_3$ . This is the method described in Frankland's *Water Analysis*, but the author prefers a solution of double the strength. He has also made use of a solution prepared by dissolving commercial potassium nitrite in alcohol, as by this solvent only the nitrite is removed, and the nitrate remains undissolved. This new method compares favourably with Griess's; when the nitrites are in large quantities, Griess's process gives a more decided reaction. The reagents are easily procured, whereas phenyldiamine is only obtained with difficulty. The exact limits of the indication have not been determined as yet, but 1 part acid in 20,000,000 parts of water can be readily detected. E. W. P.

**Estimation of Nitric Nitrogen.** By J. B. KINNEAR (*Chem. News*, **46**, 33).—The reduction of nitrates and nitrites, and conversion into ammonia by means of zinc and sulphuric acid, may be accurately accomplished if the solutions are cold and dilute; but it is advisable to use a half more of acid than is theoretically required, otherwise the



reaction is but slow; moreover, it is advantageous to fill the vessel with zinc, whereby much heat is generated, and the reaction is complete in 10 minutes; in all cases, the process must be stopped by pouring off the liquid before the acid is saturated. The ammonia may be determined in an aliquot portion by Nessler-solution, but then the zinc and acid must be pure. Lime and iron must be previously removed. Organic nitrogen does not affect the results. E. W. P.

**New Method for Determining Phosphoric Acid.** By H. PEMBERTON (*Chem. News*, **46**, 4—7).—In this new method, a standard solution of ammonium molybdate is employed to precipitate the phosphoric acid. The solution of molybdate is prepared by dissolving 89.543 grams of ammonium molybdate in water, adding a little ammonia if the solution be not clear, and then making up to 1000 c.c.; each cubic centimetre then precipitates 3 mgrms.  $P_2O_5$ . The phosphate taken should only be about 1.0 gram, and is to be dissolved in nitric acid; if silica is present, the solution must be evaporated to dryness, but the silica need not be filtered off; organic matter must be destroyed by ignition, and subsequent oxidation by nitric acid. The solution is then neutralised with ammonia, and 10 grams ammonium nitrate are added; then after heating to above  $60^\circ$ , the molybdate solution is run in, while the liquid is kept stirred; after allowing the precipitate to settle, a further quantity of molybdate is added, and so on: for the final precipitation, a small quantity may be removed and tested, as in other well-known methods. This process is not adapted for the estimation of phosphorus in iron ores, as the ferric nitrate shows a somewhat peculiar behaviour on addition of molybdate. In phosphates containing much iron, ammonia is added to the yellow solution until the colour begins to darken, and then 2 c.c. of nitric acid (1.40). Citric, tartaric, and oxalic acids interfere, but oxalic acid, if present, may be oxidised by permanganate. A single analysis requires about an hour. E. W. P.

**Estimation of Phosphoric Acid by the Molybdic Method.** By STÜNKEL, T. WETZKE, and P. WAGNER (*Zeits. Anal. Chem.*, **21**, 353—368).—The following are the details of the method, founded on a most detailed and careful investigation:—

20 to 25 c.c. of the phosphate solution, which must be free from silica, and which should contain from 0.1 to 0.2 gram  $P_2O_5$ , are mixed with so much of a concentrated solution of ammonium nitrate and of molybdic solution, that the total mixed fluid contains 15 per cent. ammonium nitrate, and not less than 50 c.c. molybdic solution to each 0.1 gram  $P_2O_5$ . The whole is then heated in a water-bath to  $80-90^\circ$ , allowed to stand for one hour, filtered, and the precipitate washed with "dilute ammonium nitrate solution." This precipitate is dissolved on the filter in 2.5 per cent. ammonia, the solution being collected in the beaker in which the precipitation took place. The whole bulk of the filtrate should amount to about 75 c.c. For 0.1 gram  $P_2O_5$ , 10 c.c. magnesia mixture is then added, *drop by drop, with constant stirring*. After two hours the precipitate is filtered off, washed with a 2 per

cent. ammonia solution, until every trace of chlorine is removed, dried, and ignited separately from the filter, the crucible being heated for 10 minutes with the flame of a Bunsen lamp, and 5 minutes by means of the blowpipe.

The strength of the various solutions referred to is as follows:—

*Molybdic solution*, 150 grams ammonium molybdate, dissolved in water, made up to 1 litre, and poured into 1 litre of nitric acid of 1·2 sp. gr.

*Concentrated ammonium nitrate solution* containing 750 grams of the salt in 1 litre.

*Dilute ammonium nitrate solution* containing 100 grams of the salt per litre.

*Magnesia mixture*: 55 grams crystallised magnesium chloride, and 70 grams ammonium chloride, dissolved in 1 litre of 2·5 per cent. ammonia solution.

O. H.

**Determination of Reverted Phosphates.** By T. S. GLADDING (*Chem. News*, 46, 18—21, 31—33).—The term “reverted” phosphate is not capable of strict chemical definition, and must be considered to refer to such as have been originally soluble, but have returned to the insoluble condition; the causes of this reversion are various, and must be considered as lying close to the border line separating soluble from insoluble, or else widely separated and different in solubility from the original insoluble form. The object of the inquiry has been to find a method of separation that shall recognise them. Fifteen series of experiments were made, and they demonstrate the various circumstances which cause the varying results so frequently obtained by analysis. Apatite, S. Carolina rock, bone-ash, Navassa and Curaçoa phosphates, were examined, and it was found that the percentage of phosphate dissolved increases very largely with increase of the solvent, or with decrease of substance taken for analysis; the solvent being 50 c.c. ammonium citrate solution, sp. gr. 1·09; time, 30 minutes; temperature, 35°. As all these phosphates are soluble more or less, it follows that errors must arise in the estimation of soluble phosphoric acid in supers containing undecomposed tricalcium phosphate, for a portion of the tricalcium salt being dissolved, the amount would be reported as “reverted.” The same results were obtained when using ammonium oxalate as a solvent. Increase of temperature is accompanied by increase of solvent power of the solvent. Owing to the solution of raw phosphates by oxalate and citrate solutions, Gruppe and Tollens recommended the employment of a 0·25 per cent. citric acid solution, as this, so they considered, dissolved like quantities of the raw material, but the author shows that it is quite incorrect. The action of different solvents of the di- and tri-basic phosphates was studied; these salts were prepared by precipitation, and mixed with calcium sulphate, so as to imitate the conditions under which they are found in supers; time, 30 minutes; temperature, 40°. Citrate solution dissolves both forms perfectly, whilst citric acid only dissolves half the quantity of the dicalcium salt that it does of the tricalcium; and dilute hydrochloric is very unsuccessful, but weak ammonium oxalate is very vigorous. The action

of citrate and oxalate on a superphosphate, made from Navassa, showed that so long as the temperature remained low ( $35^{\circ}$ ), the same amount of phosphoric acid was removed in both cases, but if the temperature was high,  $70^{\circ}$ , as in the "Cincinnati" method, a much larger percentage of phosphate was dissolved by both solutions, and the citrate dissolved more than the oxalate; the cause of this is either that the insoluble material is dissolved to a greater extent at the higher temperature, or else there is a form of reverted phosphate present which is not taken up at the lower temperature; an experiment proved that the rise of temperature had but small effect on the solution, therefore some form of reverted phosphate must be present, and arguing from the previous experiments, it must be the reverted phosphate of iron and alumina. A further set of experiments proved that these phosphates were more readily decomposed at  $70^{\circ}$ , and that for them citrate was the best solvent; as ammonium oxalate is decomposed at a high temperature, the solution becoming acid, it is necessary to conduct the solutions in stoppered flasks. It is evident then that some of the discrepancies in analytical results are in part due to the fact that citrate is but an imperfect solvent, the error increasing as larger quantities of phosphates are employed; also the discrepancy is due to the solvent action of the citrate on the crude phosphate, a larger percentage being dissolved when smaller quantities are taken. The latter cause cannot be overcome, nor is it desirable that it should be, as the purpose of the analysis is to show the amount of phosphate which can be dissolved by the liquids of the soil. It seems then necessary to fix the amounts of substance to be taken for analysis, so that the citrate shall dissolve such a percentage of the undecomposed rock in the super as shall, when reported as reverted phosphate, be a fair equivalent of its agricultural value. A modification of Fresenius' method, consisting of the use of a higher temperature, will meet the requirements of the case, provided care is taken to guard against acidity of the solvent.

E. W. P.

**Percentage of Sulphuric Acid in Red Wines.** By J. NESSLER (*Bied. Centr.*, 1882, 556).—The percentage of sulphuric acid reckoned as the potassium salt varies between 0.04 and 0.12; should the percentage rise higher, to 0.26, the extra amount will be due to the sulphur employed in the purification of the casks. A normal wine therefore contains only 1.3 gram  $K_2SO_4$  per litre, and the wine ought not to be sold if there be 1.9 gram present.

E. W. P.

**Report on the Processes of Claesson and Reis for the Determinations and Separations of Metal by Electrolysis.** By V. FRANCKEN (*Chem. News*, 46, 105—107).—To obtain accurate results, the methods recommended must be carried out most exactly. For the determination of cobalt, an excess of neutral potassium oxalate must be added, but as the oxalate is gradually decomposed by the current, cobalt carbonate is deposited with the metal; this precipitate must be removed by cautious addition of oxalic or sulphuric acid. The deposition of the metal is, however, more rapid if ammonium

oxalate replaces the potassium salt, but no more should be added than is necessary to form the soluble double salt. There is deposited with the metal a red insoluble oxide which is but slowly reduced; to prevent this, the liquid to which an excess of oxalate has been added is heated, and a further addition of 3—4 grams of solid salt is made. The cobalt forms a grey adhesive coating, which must be well washed with water, alcohol, and ether, and then dried at 100°. *Nickel* is estimated in a similar manner. In the determination of *iron*, the chloride or sulphate, with excess of ammonium oxalate, may be used, and in the reduced state it does not readily oxidise. *Zinc*, separated as above, adheres firmly to the electrode, and cannot be removed by dilute acids, but can be detached by heating the capsule to redness, and treating the residue with fresh acid. The precipitation of *manganese* is complete only when but little nitric acid is used; the presence of potassium oxalate causes separation of the peroxide, and this oxide is not firmly attached to the electrode, so that it must be separated by filtration, and converted by heat into  $Mn_3O_4$ . Ammonium oxalate must be added to *bismuth* nitrate solution, but some peroxide is formed which is but slowly reduced; great care in removing all water by alcohol and ether must be exercised, so as to prevent oxidation. The electrolytic deposition of *lead* cannot be recommended. *Copper* separates from an ammonium oxalate solution with great ease and accuracy. *Cadmium* forms a grey coating, which, although not adhering firmly, can be removed without loss if washed cautiously. *Tin* separates from the solution of chloride or oxalate as a fine grey coating. *Antimony* separates as a fine light grey firmly adhering precipitate from solutions to which sulphuretted hydrogen has been added; if the solution be acid, ammonia or ammonium sulphide in excess is added: ammonium sulphate accelerates the reduction. *Arsenic* cannot be separated quantitatively. *Iron* and *manganese* can only be separated if the formation of the manganese peroxide is prevented until the greater part of the iron has been precipitated; the presence of ammonium oxalate affects this result. If the oxalate has been decomposed before the end of the precipitation, and this is shown by the formation of a pink colour, heat must be applied, and 3—4 grams of oxalate added. If the quantity of manganese is small, it appears as peroxide at the positive electrode, but if the proportion of manganese is double that of the iron, then the peroxide must be dissolved in oxalic acid, without interruption of the current, so as to effect complete separation. The precipitation of manganese from the solution of oxalate as peroxide is not quantitative: therefore the liquid holding the greater part of the manganese peroxide in suspension, must be boiled, so as to decompose the ammonium carbonate, and then neutralised with nitric acid, after which the metal must be precipitated as sulphide. Iron and alumina are separated so long as the ammonium oxalate is in excess of the carbonate formed by electrolysis; as in the previous cases, an excess of oxalate (3 grams per 0.1 gram oxide) is added to the solution of the double oxalates, and the mixture is electrolysed whilst hot. If the alumina is in excess of the iron, the same precautions must be taken as in the case of manganese.

E. W. P.

### Influence of Gum Arabic in certain Chemical Reactions.

By J. LEFORT and P. THIBAUT (*J. Pharm. Chim.* [5], 6, 169—174).

—Mercuric sulphide is rapidly precipitated when mercuric chloride is added to the sulphur springs at Bagnères de Luchon, but if to the waters solutions of gum arabic, sarsaparilla, wild pansy, beef tea, albumin, or apple jelly be added, no precipitation will take place on addition of mercuric chloride.

It was thought interesting to study the solvent action of gum arabic on the sulphides of other metals with the view of ascertaining whether this property is peculiar to the waters of Luchon. At first, the non-precipitation of mercuric chloride was attributed to the viscosity of the solution, but this is disproved by the fact that if gum arabic be replaced by glycerol, a precipitate is produced.

Decinormal solutions of sodium sulphide and different metallic salts and a solution of gum arabic (1 to 2), were prepared. In each case 10 c.c. of the metallic solution were treated with 3 c.c. of the gum solution; and to another equal volume, 3 c.c. of distilled water was added. To each of these, 10 c.c. of the sulphide solution was added with the following results:—

	Without gum.	With gum.
Lead acetate .....	Black precipitate.	Brown solution.
Silver nitrate .....	"	Black "
Ferrous sulphate .....	"	" "
Manganese sulphate .....	Flesh-coloured precipitate.	Light brown solution.
Mercuric chloride .....	Black "	Dark " "
Copper sulphate .....	" "	" " "
Zinc sulphate .....	White "	Colourless "
Antimony trichloride + HCl ..	Orange "	Orange-coloured "
Arsenic trioxide .....	Lemon-yellow "	Lemon-yellow "

Under the above conditions, gum arabic prevents the precipitation of metallic sulphides, but in more concentrated solutions, or in presence of very small quantities of gum, precipitation, more or less incomplete, takes place.

Metallic hydrates, in presence of gum arabic, behave in a similar manner to the sulphides.

The formation of other precipitates is also prevented, as that of calcium phosphate in neutral solutions, uranium ferrocyanide, and ferric hydrate when a dilute solution of ferric chloride is treated with ammonia. The alkaloids, quinine, cinchonine, morphine, strychnine, brucine, veratrine, are not precipitated by phosphomolybdic acid, potassium mercuric iodide, or tannin, in presence of gum arabic. The non-precipitation of dilute solutions in presence of gum arabic is, however, not absolutely general, lead iodide, mercuric iodide, barium sulphate, and lead carbonate being precipitated in presence of the gum, although more slowly than when it is absent.

The intense colorations produced on adding the reagent to the metallic solutions containing gum, shows that a reaction has taken place; it therefore remains to be proved whether the precipitation is

soluble in gum arabic or held in suspension in an exceedingly fine state of division. The authors are inclined to think the latter is the more probable, since concentrated solutions of gum arabic fail to dissolve the precipitated substances even when recently formed.

From a physiological point of view, this solvent action is interesting, since it throws a light upon the existence of insoluble bodies, such as phosphates, oxide of iron, &c., in solution in the animal and vegetable juices.

It is important to notice that the ordinary method of estimating gum arabic by precipitation with lead acetate and decomposing the lead compound with sulphuretted hydrogen, cannot yield accurate results. It is better to decompose the lead compound by boiling it with a concentrated solution of ammonium carbonate.

L. T. O'S.

**Titration of Ferrous Oxide with Permanganate in Presence of Hydrochloric Acid.** By F. KESSLER (*Zeits. Anal. Chem.*, **21**, 381—383).—Priority is claimed by the author over C. Zimmermann, who recently proposed to avoid the disturbing influence of hydrochloric acid in permanganate titrations, by adding an excess of manganous sulphate; the observation, with a possible explanation of the process, having been published by Kessler 20 years ago (*Annalen*, **118**, 48).  
O. H.

**Separation of Gallium.** By L. DE BOISBAUDRAN (*Compt. rend.*, **95**, 157—160; see also this vol., p. 857).—The separation of gallium from nickel or cobalt by means of potassium hydroxide is not very satisfactory, since the precipitated nickel or cobalt hydrate obstinately retains small quantities of gallium. Calcium and barium carbonates precipitate small quantities of cobalt and nickel oxides, in addition to gallium oxide. Good results are obtained by prolonged ebullition of the strongly ammoniacal solution, if a sufficient quantity of ammonium chloride is present. The precipitated gallium hydroxide usually retains small quantities of nickel or cobalt, which may be removed by a repetition of the process. Good results are also obtained with cupric hydroxide, or with metallic copper and cuprous oxide.

Gallium may be separated from thallium by several methods, viz. :—  
(1.) By prolonged ebullition of the ammoniacal solution (sulphate, chloride, or nitrate) after reduction with sulphurous acid. (2.) By precipitation with calcium or barium carbonate in the cold, after reduction with sulphurous acid: the calcium carbonate may also be employed with a warm solution, but the precipitate then contains some thallium. (3.) If the quantity of thallium present is not too great, the gallium may be precipitated by means of potassium ferrocyanide in presence of hydrochloric acid: the precipitate is dissolved in potassium hydroxide, a small quantity of *freshly prepared* ammonium sulphide added, the thallium sulphide filtered off, and the filtrate concentrated and mixed with a large excess of hydrochloric acid and a little potassium ferrocyanide. (4.) The thallium may be precipitated as platinochloride in presence of alcohol and hydrochloric acid, but the separation is not complete. (5.) The best results are

obtained with cupric hydroxide after reduction with sulphurous acid, or with metallic copper and cuprous oxide. C. H. B.

**Estimation and Separation of Antimony and Tin.** By A. WELLER (*Annalen*, 213, 364—369).—The method employed is the same as that of Herroun (this vol., 661). Numerous analyses are given showing its accuracy. A. J. G.

**Determination of Organic Matter in Potable Water.** By J. W. MALLET (*Chem. News*, 46, 63—66, 72—75, 90—92, 101—102, 108—112).—This investigation was instituted at the instance of the American Government, and is here given in abstract: the full report has not yet been published. The object was to examine the chief processes employed for estimating the organic matter, to test the absolute and relative accuracy of the results obtained by these processes, and to ascertain the nature and scope of the practical conclusions which may be secured. The processes employed were the "combustion," "albuminoid ammonia," and the "permanganate" as suggested by Forchhammer, but in the form advocated by Tidy. The waters examined were of various qualities, good and contaminated more or less, and artificially-prepared water containing animal and vegetable matter. Each analysis was made in triplicate, and the first portion of the report gives an account of the amount of concordance observed between the analyses of each sample as obtained by each individual process; in the combustion process, there was found an average departure from the mean of an individual determination for organic carbon 2.89 per cent., for nitrogen 7.09 per cent., but the departure in some cases far exceeds these figures; however, we find that the results of the combustion process are less trustworthy for nitrogen than for carbon. The average departure from the mean in the albuminoid ammonia process was: free ammonia, 2.23 per cent.; albuminoid ammonia, 3.62 per cent. In Tidy's process the average divergence was: for oxygen consumed in one hour, 1.09 per cent.; for oxygen consumed in three hours, 0.56 per cent., showing a greater irregularity during the early stage than later. The permanganate yields, therefore, the most closely concordant results, whilst the combustion process yields the least.

*Extent of Agreement of the Results Obtained by the Different Processes with the Quantities of Organic Constituents known to be Actually Present.*—The loss of carbon by the combustion process is considerable, and there is a strong tendency to excess of nitrogen; the loss of carbon is supposed to be due to the evaporation of volatile substances such as butyric and valeric acids which have been shown to be present in some contaminated waters; the excess of nitrogen is due to the presence of ammonia compounds given off by the gas flame in the neighbourhood of the evaporating liquid; for although carefully covered, yet there is still a slight communication with the outside air by means of the notch in the rim of the water-bath for the passage of the feed-flask neck. Suggestions are made so as to show how this access of ammonia may be prevented by evaporating the water by steam, by evaporating the water in a vacuum, &c. The loss of nitrogen in

Wanklyn's process is due to volatilisation of the amines during the first distillation, and as these compounds are not indicated by Nessler, they escape detection as "free" or as "albuminoid" ammonia. In order, therefore, to diminish this loss, a separate distillation should be made with alkaline permanganate added at once; also to avoid the uncertain ending of the collection of ammonia, the distillation should not be stopped until the last measure of distillate contains less than 1 per cent. of the whole ammonia already collected; several other alterations in the details of the process are also recommended. The analytical figures obtained by Tidy's process show that the putrescent substances are accurately determined, but not so the non-putrescent, as their oxidation by cold permanganate is so slow; on the other hand, by Kubel's method (oxidation at  $100^{\circ}$ ), a loss of volatile matter occurs; it is proposed, therefore, to extend the time of oxidation to 12 or 24 hours at a temperature of  $20^{\circ}$ , examinations of the amount of oxidation being made at intervals of 1, 3, 6, and 9 hours.

*Effect on the Results of the Different Processes by Varying the Extent of Dilution of the same Organic Substances in Water.*—Under this heading, we find that the weaker the solution, the greater is the loss of carbon during evaporation, but the greater is the gain in nitrogen; hence, when applying Frankland's ratio C:N to a dilute water, the pollution would appear to be of animal origin; but the stronger the water is, the greater will be the tendency to refer the contamination to a vegetable source. In reference to Wanklyn's process, the weaker the solutions are, the higher are the results obtained for ammonia in both forms. The influence of dilution on Tidy's process is far less marked, but stronger solutions require somewhat less oxygen than is required by calculation. Among the special conclusions drawn concerning Frankland's process, we find that the formation of sulphuric acid from the sulphurous acid added during evaporation is of more frequent occurrence than is generally supposed. The combustion process, in its present form, cannot be considered as determining the carbon and nitrogen in water absolutely, as it is but as a method of approximation; but in many cases its indications of organic carbon are more valuable than those of the permanganate process, and its results for organic nitrogen more valuable than the indications afforded by the albuminoid ammonia process. The value of Wanklyn's process depends more on watching the rate and progress of evolution of the ammonia, than upon the determination of the total amount. The results obtained by Tidy's process are liable to variation with atmospheric temperature at the time of examination, and the amount of oxygen consumed is not a measure of the carbon present. The value of the results depends, as in the ammonia process, more on watching the rate and progress of the oxidation, than on the absolute amount of oxygen consumed.

*General Remarks on other Chemical Determinations.*—The estimation of total solids is liable to great error because of the large effect produced by slight differences in the dryness attained, or by atmospheric deposition on the platinum basin. Waters containing a high percentage of nitrates generally contain but little ammonia; Frankland's view that nitrates are not found in waters deficient in oxygen is in



accordance with the results now obtained, with a few exceptions; nitrates are not always formed by reduction.

As the amount of carbon and nitrogen is so excessively small in any ordinary contaminated water, evil effects resulting from the use of such a water cannot be due to chemical compounds, but rather to living organisms present at the same time; the presence of nitrates is not sufficient evidence for the condemnation of a water, but rather that of nitrites, which may be due to a special ferment, which is itself capable of propagating disease. From the presence of chlorides, contamination by animal or vegetable matter must only be determined with great caution. At present, attempts to determine the source of the contamination, whether animal or vegetable, have not been followed by very satisfactory results. Biological experiments show that such waters as are dangerous to animal life have a high C:N ratio. Tidy considers that the putrescent or easily oxidisable substances are of animal origin, whereas those less easily putrescent are vegetable matters; the author does not wholly agree with him, as he finds that the proportionate consumption of oxygen within the first hour is rather greater for those waters containing vegetable than for those containing animal matter, whilst one of the co-workers in this investigation—Smart—considers that the gradual evolution of albuminoid ammonia (Wanklyn's process) indicates organic matter, whether vegetable or animal, in a fresh condition, whereas a rapid evolution indicates putrescent organic matter. Finally, it is not possible to decide absolutely on the wholesomeness of a water by the mere estimation of organic matter. All samples should be examined without delay, as great changes may occur in the composition of the water, but samples should also be kept for 10 or 12 days, and then examined, and their composition compared with that of the fresh sample.

E. W. P.

**Determination of Sulphur in Coal-gas.** By O. KNUBLAUCH (*Zeits. Anal. Chem.*, **21**, 335—353).—Valentin's method and apparatus for sulphur estimation in gas is criticised and modified by the author. He dispenses with the gas-meter, the platinum tube, and potassium carbonate essential to Valentin's method, and substitutes for them a graduated aspirator, glass tubes, or platinised asbestos, and works on much smaller volumes of gas. Numerous results of test experiments are given.

O. H.

**Flashing Point of Petroleum.** By L. LIEBERMANN (*Zeits. Anal. Chem.*, **21**, 321—329 and 329—335).—Instead of the complicated and often imperfect contrivances now in use to ascertain the flashing point of petroleum, the author proposes to heat the hydrocarbon in a water-bath, and to blow air through the liquid, applying a light at intervals of every degree temperature. He furnishes numerous experimental data, showing that the amount of hydrocarbon employed does not influence the results, the latter being very constant.

In the second paper, the author draws attention to the fact that in petroleum lamps, after the lamp has been alight for some time, the hydrocarbon becomes from 2.5° to 9° C. warmer at the top of the oil vessel nearest to the flame than at the bottom. The maximum of air

temperature observed in Europe being  $50^{\circ}$  C., he concludes that paraffins oils intended for use in Europe should have a flashing point of at least  $60^{\circ}$ . O. H.

**Quantitative Estimation of Fusel Oil in Brandy.** By L. MARQUARDT (*Ber.*, 15, 1661—1665).—The chloroform used in the author's method for estimating fusel oil (*Ber.*, 15, 1370, this vol., 1235) must be purified by treatment with potassium dichromate mixture. The presence of fusel oil in brandy can easily be detected by shaking 30 c.c. of the diluted spirit with 15 c.c. of pure chloroform. The chloroform is decanted, washed once with water, and allowed to evaporate at the ordinary temperature. Water containing 2 drops of sulphuric acid is poured on the residue, sufficient potassium permanganate is added to impart a red coloration to the liquid, and the mixture is left in a closed vessel for 24 hours, when the odour of valeric acid will be perceptible, if the sample of brandy contains fusel oil.

W. C. W.

**Estimation of Astringent Substances in Wines.** By A. GIRARD (*Compt. rend.*, 95, 185—187).—To absorb the tannin and colouring matters, the author employs sheep-gut, such as is used for the manufacture of violin strings. The gut is well washed, freed from foreign tissues, treated with alkalis, and bleached by the action of potassium permanganate and sulphurous acid. It is then twisted into cords and again bleached by the action of gaseous sulphurous anhydride. This treatment is precisely the same as that adopted in the preparation of violin strings, except that the final treatment with oil is omitted.

From 3 to 5 grams of the gut-cords, the water in which has been previously determined, are soaked in water for four or five hours, the cords untwisted, and the gut added to 100 c.c. of wine previously diluted with water if necessary. After from 24 to 48 hours the whole of the tannin and colouring matter is absorbed, whilst the alcohol, glycerol, gum, succinic acid, &c., remain in solution. The gut is removed, washed two or three times with distilled water, dried at  $35-40^{\circ}$ , then transferred to a stoppered vessel, dried at  $100^{\circ}$ , and weighed. The increase in weight of the dried gut gives the amount of tannin and colouring matter contained in the wine. C. H. B.

**Detection of Adulterated or Artificial Honey.** By PLANTAREICHENAU (*Bied. Centr.*, 1882, 575).—In one-half of the sample of honey, the grape-sugar is to be estimated; in the other half, the same substance must be determined, after treatment of that portion with 2 per cent. sulphuric acid; and in a separate portion dextrin is to be precipitated by alcohol. The difference between the first and second estimation is so great that there is no difficulty in determining whether it is an adulterated sample. E. W. P.

**Analysis of Dynamite.** By G. LUNGE (*Dingl. polyt. J.*, 245, 171—173).—The author mentions that the method of extracting nitroglycerol by means of solvents, and weighing it after drying, is known to give rise to errors, and is applicable only in the case of the simple guhr-dynamite. For the more complex dynamites, it is best to

determine the nitrogen present, which may be effected by the use of the author's nitrometer for estimating acids, or the recently constructed nitrometer for the estimation of potassium nitrate (*ibid.*, 243, 421). Nitroglycerol containing nitrocellulose may also be analysed in the nitrometer by dissolving a weighed sample in sulphuric acid and sucking the solution into the apparatus. In this case, the total quantity of nitrogen is obtained, the nitrogen present in the nitroglycerol being determined by treating in the nitrometer a certain quantity of the extract yielded by the dynamite to anhydrous ether. Dynamites prepared with cellulose, however, are more readily analysed by extraction with ether in a Soxhlet apparatus. For the estimation of the nitrogen in the so-called Trauzl dynamite (nitroglycerol, cellulose, and potassium nitrate) the following method is recommended:—About 10 grams are desiccated for 24 hours and the moisture is determined by the difference in weight. The mass is then extracted with anhydrous ether and the percentage dissolved is estimated by weighing the extract which presumably consists of nitroglycerol. A small portion of this is analysed in the nitrometer and the percentage of pure nitroglycerol calculated. The residue insoluble in ether is washed with hot water and weighed, having been previously dried at 70–80° and for 24 hours in a desiccator. It consists of cellulose containing at times nitrocellulose (1–2 per cent.).

In conclusion, the author mentions that he made some experiments, and found that, unlike ethereal nitro-compounds, nitro-compounds when shaken with sulphuric acid and mercury do not evolve their nitrogen as nitric oxide.

D. B.

**Creosote from Beech-tar.** (*Dingl. polyt. J.*, 245, 91.) According to Hartmann and Hauers, pure creosote from beech-wood tar consists of guaiacol and cresol, and forms a neutral clear pale yellow strongly refractive liquid having a smoky smell. Its sp. gr. is 1.07 at 15.6°; it boils at 205–225° and dissolves in 200 parts of water. By mixing 2 c.c. of the creosote with 8 c.c. of water and 2 c.c. soda-ley (sp. gr. 1.33), a light yellow perfectly clear solution should be obtained, and a similar result with light petroleum. If the mixture does not dissolve, it indicates the presence of considerable quantities of phenol and cresol. By adding a few drops of water to the solution and shaking it vigorously, no separation should be effected. If it occurs, it may be recognised as an oily layer suspended between the petroleum and the water. In this case also, phenol and cresol are present, although in smaller quantities. If, on mixing the same solution with about 4 c.c. of a cold saturated solution of barium hydroxide, the petroleum assumes a blue colour and the aqueous solution turns red, the creosote contains oily bye-products. When a mixture of 2 c.c. creosote and 2 c.c. collodion is shaken, no signs of a gelatinous precipitate should be observed. From a mixture of 9 c.c. glycerol of sp. gr. 1.23, 3 c.c. water, and 4 c.c. creosote, the latter separates completely after a time.

D. B.

**Action of Potassium Permanganate on Benzoic Acid, &c.** By C. LEUKEN (*Arch. Pharm.* [3], 20, 518–524).—The author worked

with a solution containing 23.5 grams potassium permanganate and 30.0 grams pure sodium hydroxide to the litre. He found that 0.1 gram of chemically pure benzoic acid used 0.4 c.c. of this solution; other less pure samples of benzoic acid required somewhat more.

The author confirms Schneider (*Pharm. Zeitung*, 1882, 273) in his statement that 0.01 gram of vanillin requires 0.051 gram potassium permanganate (the author found 0.06). This agrees with a complete oxidation of vanillin. Salicylic acid offers another example of complete oxidation by potassium permanganate.

F. L. T.

### Estimation of Tartaric Acid in Tartar and in Wine Lees.

By P. CARLES (*J. Pharm. Chim.* [5], 5, 604—606).—The method of estimating the value of tartar is detailed, as well as that for determining the amount of calcium tartrate in the wine lees and plaster residues, by treating with hydrochloric acid, filtering, and precipitating the calcium tartrate in the filtrate with ammonia. In this method, it has been held that calcium tartrate is soluble to an appreciable extent in ammonium chloride; so that when the use of a large excess of hydrochloric acid is necessitated by the presence of foreign bodies, the results are too low. To determine the effect of excess of hydrochloric acid, the author estimates the amount of calcium tartrate left in solution by concentrating and mixing it with twice its volume of alcohol and weighing the calcium tartrate precipitated.

The following table shows the results:—

Calcium tartrate .....	4	4	4	4
„ sulphate .....	0	0	1	1
Water .....	25 c.c.	25 c.c.	25 c.c.	25 c.c.
Hydrochloric acid .....	50 „	100 „	50 „	100 „
Water to wash the precipitate and to make a vol. of .....	50 „	50 „	50 „	50 „
Ammonia Q.S.				
Precipitated after 2 hours; dried at 100° ..	3.735	3.765	3.805	3.763
Precipitated after 12 hours after addition of 50 c.c. alcohol 90°	0.033	0.035	0.050	0.075
Precipitated after 12 hours after addition of 50 c.c. alcohol	0.152	0.170	0.213	0.190
Total .....	3.920	3.970	4.068	4.028
Loss per cent. ....	2.000	0.750	—	—
Excess per cent. ....	—	—	1.70	0.70

L. T. O'S.

**Aldehyde Reaction with Ammoniacal Silver Nitrate Solution.** By E. SALKOWSKI (*Ber.*, 15, 1738—1739).—The ammoniacal silver nitrate solution containing soda, which is recommended by Tollens (following abstract) as a reagent for aldehyde, has the disadvantage of depositing silver fulminate.

W. C. W.

**Silver Solution as a Reagent for Aldehyde.** By B. TOLLENS (*Ber.*, 15, 1635—1639).—Ammoniacal silver nitrate solution is rendered more sensitive to aldehyde and glucose by the presence of potash or soda. The reagent is prepared by dissolving 3 grams of silver

nitrate in 30 grams of ammonia (sp. gr. 0.923). To this is added 3 grams of soda in sticks, dissolved in 30 grams of water. The solution must be kept in the dark in stoppered bottles, as it deposits silver fulminate on prolonged exposure to the atmosphere.

This reagent immediately yields a mirror with a liquid containing 1 per cent. of aldehyde, and in half a minute with a solution containing 0.1. One part of aldehyde in 10,000 of water yields a yellow-brown mirror in five minutes.

Solutions of dextrose of varying strengths gave the following results:—1 in 1000 mirror in a quarter of an hour, 1 in 10,000 in two hours, 1 in 50,000 gave a faint mirror in 24 hours.

This silver solution is also reduced by milk-sugar at the ordinary temperature, and by pure cane-sugar when the mixture is warmed.

W. C. W.

**Estimation of the Nitrogenous Constituents of Urine.** By H. BYASSON (*J. Pharm. Chim.* [5], 6, 20–26).—The constituents of urine are divided into 4 classes:—(1) urea; (2) uric acid; (3) the other nitrogenous bodies, creatine, creatinine, leucine, tyrosine, and hippuric acid, called extractive substances; and (4) ternary substances, glucose, inosite, lactic acid, &c.

It is shown that whenever urine is treated with sodium hypobromite, not only is the urea attacked with evolution of nitrogen, but, on standing, also uric acid and the other nitrogenous bodies: thus, after two minutes, 3 mgrms. of uric acid evolved 1 c.c. nitrogen.

To avoid this error and enable a complete and rapid analysis of urine to be made, the following method is proposed:—5 c.c. of urine are acidified with sulphuric acid, warmed, and titrated with a millinormal solution of potassium permanganate, which oxidises the ternary substances and all nitrogenous bodies, except urea. After this treatment, the urea in the urine is estimated with sodium hypobromite. 5 c.c. of urine are then treated with 20 c.c. of a solution of mercuric nitrate, containing 72 grams HgO per litre, which precipitates all the nitrogenous bodies. The solution is next treated with sodium carbonate, filtered, and the filtrate acidified with sulphuric acid, the ternary substances are estimated by titration with potassium permanganate solution. The difference between this and the permanganate used in the first operation gives that required to oxidise the nitrogenous substances.

The uric acid is estimated by acidifying with  $\text{H}_2\text{SO}_4$  and 50 c.c. of urine, and adding baryta-water in excess, which precipitates the uric acid completely along with the phosphates and sulphates, &c. The precipitate is washed, introduced into a flask, and treated with sulphuric acid. The uric acid is then determined by means of permanganate solution.

1 c.c. of a millinormal permanganate solution equals 3.333 mgrm. of nitrogenous substances, analogous to uric acid and creatinine, and to 0.2 mgrm. of ternary substances as glucose and lactic acid. These being known, it is easy to calculate the amounts of the different substances present.

For the estimation of the urea, Regnard's apparatus is preferred.

It is of importance that after addition of the permanganate solution,

the urine should be warmed to aid the reaction, but not boiled, which causes the precipitation of the manganese. L. T. O'S.

**Estimation of Pollen in Hops.** By R. BRAUNGART (*Bied. Centr.*, 1882, 573).—By a method which is kept secret, the pollen present, and which amounts to 3·76—19·346 per cent., can be easily and rapidly determined. E. W. P.

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## Technical Chemistry.

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**Separation of Ammonia from Gas.** (*Dingl. polyt. J.*, **245**, 40—42).—For the removal of ammonia from common gas in the dry way, Bolton and Wauklyn propose to pass the gas freed from tar through a purifier containing layers of superphosphate spread on hurdles. Ammonium superphosphate is formed, which is used for manuring purposes.

Bunte describes a series of experiments in which 1500 k. of Mejillones superphosphate, containing 18·7 per cent. soluble phosphoric acid, were spread on the ground and moistened with 75 litres of gas liquor. Thus the free sulphuric acid present in the superphosphate, which, by absorbing the heavy hydrocarbons, affects the illuminating power of the gas, is neutralised and the mass rendered porous, and its absorptive power increased by the evolution of gas (carbonic anhydride and sulphuretted hydrogen). The superphosphate was introduced into an ordinary purifier and spread on sawdust to a depth of 10—15 cm. The gas on leaving the purifier contained 0·56 g. ammonia per 100 cubic meters, that on entering from the scrubbers containing 60 g. Subsequently a cylindrical chamber 3 inches in diameter and 2 inches in height was used, the superphosphate being laid on the upper trays and sawdust beneath. The gas containing 97 g. of ammonia in 100 cubic meters, after passing through this chamber, was purified, and the quantity of ammonia reduced to 1—2 g. From a number of experiments, the quantities of ammonia in 100 cubic meters of gas were as follows:—Hydraulic main, 427 g.; before passing through condenser, 388; before the scrubbers, 220; after the scrubbers, 59·5; after the superphosphate, 3·4. The ammoniacal water contained 19·2 g. ammonia per litre. The quantity of ammonia in the purifier increases with the degree of saturation of the superphosphate; it is, therefore, necessary to renew the contents of the purifier as soon as the gas contains large quantities of ammonia.

D. B.

**Consumption of Fuel in House Stoves.** By F. BODE (*Dingl. polyt. J.*, **245**, 31—35 and 81—86).—The experiments which form the subject of the present paper were made with an American stove similar in construction to the house stove described and illustrated by Meidinger (*ibid.*, **225**, 203). After giving a detailed account of the

different parts of the stove, the author proceeds to describe the results and conclusions arrived at. The fuel used is Pennsylvanian anthracite of the following composition, the coal being dried at 105° in a current of carbonic anhydride:—

C.	H.	N and O.	Ash.
86.91	2.80	3.89	5.97

The total sulphur was 0.57, of which 0.43 was volatile, and 0.14 contained in the ash. By taking the percentage of nitrogen at 0.89, disregarding the sulphur in the ash and adding 1 per cent. for moisture, 1 kilo. of anthracite gives the following products on burning:—

	Kilo.	Products. k.	Oxygen required. k.
Carbon.....	0.8604	CO <sub>2</sub> .. 3.155	2.294
Hydrogen....	0.0277	H <sub>2</sub> O . 0.249	0.222
Oxygen.....	0.0300		
Nitrogen ....	0.0085	N ... 0.008	—
Sulphur ....	0.0043	SO <sub>2</sub> .. 0.009	0.004
Ash .....	0.0591		
Moisture ....	0.0100	H <sub>2</sub> O . 0.010	—
	<hr/> 1.0000	<hr/> 3.431	<hr/> 2.520
		Oxygen contained in coal..	0.030
			<hr/> 2.490

The author was unable to determine the heat evolved calorimetrically, the numbers quoted being obtained by calculation.  $(0.8604 \times 8080 + 0.0277 \times 29630 + 0.0043 \times 2222) - 0.01 \times 640 = 7777$ . For the heat of combustion of hydrogen, 29630 was taken, as 34462, the number usually employed, embraces the heat liberated by the condensation of the water formed, and in the case under consideration this amount is not included. With a view of determining the amount of heat given to the air of the room and that escaping into the chimney, and comparing the results with the calculated values, a series of gas analyses was made. During the analyses, the temperature of the room ranged between 14° and 21°. The results, which are embodied in a number of tables, seem to show that the formation of carbonic oxide is very small; in fact, so small that for calorimetric purposes it may be entirely ignored. It is further proved, that with moderate firing and a slight draught, the loss of heat amounts to 44 per cent.; whilst a strong fire and an increase in the current of air reduces the loss to 29 per cent. of the theoretical heating effect.

D. B.

**Ventilation of Laboratories.** By J. BING (*J. pr. Chem.* [2], **26**, 131—143).—The author discusses this matter from a hygienic point of view, and thinks it of very great importance that the noxious and poisonous gases of the laboratory should be got rid of, and that the atmosphere should always be supplied with the requisite amount of oxygen.

D. A. L.



**Harmful Constituents of Furnace Gases, and their Removal.**

By M. FREYTAG (*Bied. Centr.*, 1882, 505—510).—The damage done to plants by furnace gases is well known, and it was attributed by Stöckhardt to the sulphurous anhydride and to the metallic particles, especially lead oxide, present. The author, however, holds a different opinion, and considers that the principal damage is due to the sulphuric acid and soluble sulphates, and that the action of sulphurous anhydride is indirect, being absorbed by the moist leaves and oxidised to sulphuric acid by oxygen under influence of sunlight. No direct damage is done to the soil by the floating metallic particles, but settling as they do on the leaves of fodder plants, they induce disease in the animals feeding on those plants. The leaves damaged by gases appear spotted or striped, and when the damage is severe, they curl up and die; the plant then continues to throw out fresh leaves, which are also killed, and exhaustion ensues. Moreover, as assimilation is interfered with, the plant dies from above downwards, and the roots throw out fresh shoots. Blossom, when affected, cannot produce seed; young and soft leaves are more readily affected than those with a hard epidermis. Moisture, direction of wind, temperature, intensity of light, and configuration of the land determine the area of country affected; the greatest damage is done in the mornings and nights, when the fumes descend on bedewed plants. False diagnosis must be guarded against, as the damage done by gases closely resembles that done by frost and parasites. The action of sulphuric acid fumes on the soil is not harmful, as gypsum is generally formed; but although the dust of copper, zinc, &c., works, does no direct damage to the plants, yet by preserving the dead leaves, the formation of humus is hindered. The percentage of sulphates in damaged plants is thrice that found in healthy plants of the same kind. The Glover and Gay-Lussac towers being insufficient to keep back all the harmful gases, it is recommended to pass the mixed gases into lead chambers, into which a spray of concentrated sulphuric acid is introduced. This removes 96·7 per cent. of sulphuric acid and 66 per cent. of the sulphurous anhydride. Should this be insufficient, the gases must then be passed through a chamber containing diluted sulphuric acid (chamber acid). With regard to flue-dust, Reich has shown that 10 per cent. of the molten ore is removed in this way, and this dust contains 50 per cent. "anhydrous vitriol" and 7·5 per cent. arsenious anhydride. Experiments to test the effect of dry and moist sulphur dioxide on wheat, peas, oats, and beet were made, with the following results:—Chlorophyll is destroyed by sulphur dioxide in moist air when the ratio of the volumes is 1 : 55,000, but no harm seemed to be done when the ratio was 1 : 75,000. Sprinkling with water containing 0·02 per cent. sulphur dioxide, did no harm; a stronger solution of 0·08 per cent. only did damage when a warm wind was blowing, whereby the solution became concentrated; sulphuric acid produced results similar to those from sulphurous anhydride; sulphites could not be detected in the leaves, only sulphates; dry air containing 0·25 per cent. sulphur dioxide produces no results. The author considers that 9—12 per cent. of the sulphur present in the gas is combined as  $\text{SO}_3$ , formed by the ozonising of sulphurous anhydride, by the passage of sul-

phurous anhydride and oxygen over heated materials in the furnace, and by the dissociation of sulphuric acid at a red heat.

E. W. P.

**Preparation of Basic Furnace Linings.** (*Dingl. polyt. J.*, **245**, 94.)—For furnace linings Kutscha, Oelwein, and Mertens recommend the use of the mineral agalmatolite, occurring at Dilln, near Schemnitz, in Hungary. Its composition is—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MnO.	CaO.	MgO.	SO <sub>3</sub> .	H <sub>2</sub> O.	Alkalis.
30·40	52·68	0·80	0·30	0·89	0·39	0·80	11·88	1·50

By mixing 2 parts of burnt agalmatolite with 1 part of the raw mineral, and moistening the mass with water, the mixture may be pressed into briquettes, which on burning at a white heat become hard and adhesive, and do not shrink. For the preparation of basic linings, it is proposed to add to lime or dolomite a flux in such proportion that the mixture after 12 hours' burning at a white heat forms a slag, which is pulverised and worked up with suitable binding agents. For the manufacture of such basic refractory masses, dolomite of the following composition is used:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	CO <sub>2</sub> .
0·7	0·5	0·6	31·5	20·0	46·7

mixed with 12 per cent. of talc of the composition—

SiO <sub>2</sub> .	MgO.	FeO.	H <sub>2</sub> O.
62·0	31·0	2·0	5·0

The mixture is formed into bricks, heated for 12 hours at a white heat, pulverised, treated with 5—8 per cent. tar, 3—5 per cent. pitch, or 5—10 per cent. rosin, pressed whilst hot in heated moulds, and burnt at a high temperature.

Bollinger recommends the use of a mixture of asbestos, chrysolite, and magnesium chloride for the preparation of refractory basic linings.

D. B.

**Formation of Patina.** By R. WEBER (*Dingl. polyt. J.*, **245**, 86—91, 125—131, 176—183, and 256—264).—It is well known that bronze statues erected in large towns assume a dark appearance resembling that of iron, whilst the number of bronzes which are coated with a green film known as patina is very limited. This coating differs from the black film usually observed by its pleasing colour, smoothness, and transparency, so that the bronzy metal under the film is visible in some places, the result produced being very effective. The conditions which favour the formation of this green film are a pure atmosphere, the presence of moisture in the air, a smooth surface, and the composition of the metal forming the bronze. While zinc alloys (brass) assume a black irony appearance in moist air, tin alloys (bronze) are less readily oxidised. Nevertheless zinc is largely used for the production of metallic statues, probably owing to the assumption that the casting of such alloys is effected with greater ease, and that the material is worked more readily. Ancient bronzes,

however, and some of modern date containing only small quantities of zinc, afford proof to the fact that it is possible to overcome the difficulties experienced in casting, &c., without the use of large quantities of zinc. The author attributes the formation of this green film mainly to the composition of the alloy, and suggests that the quantity of zinc used should be limited as much as possible.

D. B.

**Action of Cement on Lead Pipes.** By M. BAMBERGER (*Dingl. polyt. J.*, **245**, 35).—The author had occasion to examine a piece of lead pipe which had rested for five years in a layer of Portland cement. It was coated with a red layer, 1 to 3 mm. in thickness, resembling litharge in appearance. This film was removed carefully. Its sp. gr. was between 8·002 and 9·670, the difference being due to the presence of adhering metallic particles of lead and lead carbonate. The following is the composition of the film:—

PbO.	Pb.	H <sub>2</sub> O.	CO <sub>2</sub> .	CaO.	Matter insoluble in nitric acid.
84·89	12·33	0·99	1·53	traces	0·16

This coating seems to have been produced by the action of the oxygen of the air in conjunction with that of the lime contained in the mortar. According to Besnou (*ibid.*, **219**, 459), lead is attacked considerably by lime-water.

D. B.

**Purification of Beet Spirit.** By L. SALZER (*Bied. Centr.*, 1882, 574).—According to this patent, 80 grams pure potassium hydroxide are left in contact with every hectolitre of 90 per cent. alcohol, with frequent stirring during the first 24 hours; then 10 per cent. of water is added, and the whole stirred for 36 hours. Filtration and neutralisation with tartaric acid follows, after which pure alcohol may be distilled off.

E. W. P.

**Composition of Wines from Marc.** By A. GIRARD (*Compt. rend.*, **95**, 227—232).—A considerable quantity of wine is now made by covering the marc with an aqueous solution of sugar, and allowing the mixture to ferment. The sugar solution contains 18 grams per litre for every degree of alcohol which it is desired to obtain, and 250 grams of marc are used for each litre of solution. Analyses of wines prepared in this way by the author himself, and of other samples found in commerce, prove that these wines have an approximately definite composition. When they contain from 9 to 10 degrees of alcohol, the proportion of soluble matter, cream of tartar, tannin, and colouring matter is much less than in the ordinary vintage wines. The amount of solid matter varies from 14 to 18 grams per litre; the amount of cream of tartar is about 2 grams, but not less than 1·6 gram per litre, whilst the proportion of tannin and colouring matter varies considerably with the nature of the marc. No advantage is gained by allowing the liquid to remain in contact with the marc after fermentation has ceased; on the contrary, the proportion of solid matter, &c., is diminished. No advantage is gained by increasing the proportion of marc per litre of sugar solution, but the amount of colouring

matter and tannin is considerably increased by mixing the marc with the stalks of the grapes. The author concludes that these wines constitute a highly useful beverage, and can be produced at a very low cost.

C. H. B.

**Plastering and Deplastering of Wines.** By P. CARLES (*J. Pharm. Chim.* [5], 6, 118—123).—The author discusses the question of plastering wines from a hygienic point of view, showing how the use of gypsum to clear the wines renders them hurtful as beverages. The calcium sulphate acts on the potassium bitartrate in the juice of the grape, forming calcium tartrate, tartaric acid, and potassium sulphate, a large proportion of the last two bodies remaining in the wine. Without plastering, wine contains about 2 grams per litre of free tartaric acid, whilst after plastering it contains double or treble that amount, and even more, according to the quantity of potassium bitartrate decomposed. The quantity of potassium sulphate amounts to from 4 to 7.5 grams per litre. Owing to the purgative properties of this salt, the author is of opinion that the quantity present should not exceed 2 grams per litre.

That sulphuric acid is not found in abnormal quantities in the ashes of wines is explained by the fact that when the wine containing tartaric acid and potassium sulphate is evaporated, the latter is decomposed, with the liberation of sulphuric acid, which is expelled on ignition of the residue, and alkaline carbonates remain behind.

Owing to the injurious nature of the impurities in plastered wines, endeavours have been made to free them from these by a method called deplastering, but the remedy proves worse than the defect, since samples of deplastered wines which the author has analysed are shown to contain barium salts, barium chloride being used to remove the sulphuric acid. In some cases, excess of the barium salt was found in the wine, and in others barium sulphate was held in suspension. The use of barium salts is therefore to be deprecated—(1) because of the uncertainty of ensuring the employment of the exact quantity of barium salt for the decomposition of the sulphate; (2) owing to the extreme state of division of the precipitated barium sulphate, it is impossible to completely free the wine from it; consequently the wood of the barrels becomes impregnated with the sulphate, from which it is impossible to free them by washing.

L. T. O'S.

**Amount of Sulphurous Acid necessary to Prevent the Formation of "Mother" in Wine.** By J. MORITZ (*Bied. Centr.*, 1882, 555).—Experimentally it has been shown that for every 600-litre wine cask, the burning of 20 grams sulphur, and even less, is sufficient to destroy the action of *Mycoderma vini*.

E. W. P.

**Beet-root Wine.** By J. LEFORT (*J. Pharm. Chim.* [5], 5, 581—583).—Owing to the ravages of the phylloxera among the vines, substitutes for grape-juice are being introduced for the manufacture of wines; of these the author specially condemns the use of beet-root sugar, since during its fermentation, besides ethyl alcohol and aldehyde, it yields propyl, butyl, and amyl alcohols, which have been shown

by Dujardin and Audigé to act as poisons in very small quantities. Betaine is also produced to the amount of 1 to 5 per cent. A kilogram of red beet-root after being made into a pulp with warm water, and the extract subjected to fermentation, in three days yielded a pale red liquid, containing 4 to 5 per cent. alcohol, having a very disagreeable taste, and retaining the odour of beet-root.

L. T. O'S.

**Gelatinised Grain for Brewing.** By J. BERSCH (*Bied. Centr.*, 1882, 574).—The grain is first steeped, then heated under pressure with steam, whereby the starch is caused to swell and form a firm paste; should the temperature rise, soluble starch-sugar and peptones are formed. The steamed grain is then dried and powdered, and may be used in place of malt, from which it differs by its want of aromatic constituents.

E. W. P.

**Effect of Adding Soda or Acid to the Water used for Seasoning Casks.** By J. MORITZ (*Bied. Centr.*, 1882, 574).—By the addition of soda, more substance is removed from the wood of the casks than when acid is used; but less is removed if the wood is introduced into the cold solution, and the whole is then heated.

E. W. P.

**Purification of Beet-juice by Means of Sulphurous Anhydride and Filtration through Gravel.** (*Dingl. polyt. J.*, 245, 264).—According to Reinecke and Stutzer, the juice obtained by diffusion is treated at 68° with 1·8 per cent. calcium hydroxide; saturated with carbonic anhydride to an alkalinity of 0·14—0·18 per cent.; and forced through filter-presses by means of steam pressure. The clear juice is again mixed with calcium hydroxide, the alkalinity reduced to 0·08—0·10, boiled, and the mass treated as before. A current of sulphurous anhydride is then introduced into the juice running from the presses and the resulting solution passed through a filter filled with gravel. The filling mass obtained according to this method contained about 67·8 per cent. of first product, which consisted of 95 per cent. sugar, 1·8 per cent. water, 1·6 per cent. bases, and 1·6 per cent. organic non-saccharine matters. The second product and the molasses therefrom contained—

	Second product.	Molasses.
Sugar .....	88·9	55·74
Water .....	3·4	19·65
Bases .....	3·8	10·80
Non-saccharine organic matter	3·9	13·81

The bases contained 14·84 and 9·46 per cent. sulphuric acid, and the molasses 0·61 per cent. invert-sugar.

Drenckman and Crahe are of opinion that for juice of inferior quality the old process (purification by means of animal charcoal) is the most advantageous.

D. B.

**Application of Sulphurous Anhydride in Bleaching.** By M. MOYRET (*Dingl. polyt. J.*, 245, 183).—The author describes a process of bleaching silk, wool, animal fibres and straw by means of sulphurous

anhydride. Vegetable fibres being attacked cannot be bleached with this agent, but chlorine may be used with advantage in such cases. For bleaching animal fibres, gaseous sulphurous acid or bisulphites are used or liquid sulphurous acid, the latter, however, acts less energetically. The goods after washing and wringing in a centrifugal machine, are brought whilst damp into a closed chamber and covered with a thick cloth. They are then exposed to the action of sulphurous anhydride liberated by burning sulphur in a crucible placed in the corner of the chamber. According to the purity of whiteness required, the operation is continued for from 12—24 hours or more. The goods are then rinsed in lukewarm dilute hydrochloric acid to remove any particles of sulphur deposited thereon. For bleaching loose wool, a solution of sodium bisulphite is used, the wool being subsequently passed through lukewarm hydrochloric acid, whereby sulphurous anhydride is evolved in a nascent state, and bleaches the wool.

D. B.

**Use of Electrolysis in Dyeing and Printing.** By F. GOPPELS-ROEDER (*Compt. rend.*, 95, 239—241).—To produce aniline black on fabrics or on paper, the latter is impregnated with an aniline salt, preferably the hydrochloride, and placed on an indifferent metallic plate, which is in contact with one pole of a battery or small dynamo-machine. A second plate, which is in contact with the other pole, and on which is traced the design or writing to be printed, is pressed down upon the fabric, and the current allowed to pass. A copy of the design in black is thus obtained. Medals and coins may also be reproduced. Further, it is easy to write with a pencil consisting of an indifferent metal or of carbon, and forming one of the poles, on a fabric or on paper impregnated with an aniline salt and placed upon a metallic plate, which forms the other pole. Whenever the pencil touches the fabric the current passes, and aniline black is produced. The author has succeeded in producing in the same way other colours which are readily formed by dehydrogenation or oxidation.

To remove colours, such as Turkey-red or indigo already fixed upon a fabric, the latter is impregnated with a solution of a nitrate or chloride. Chlorine or nitric acid is liberated at the positive pole and oxidises the colouring matter, forming colourless products. If salts are used, the bases of which can act as mordants, it is possible by means of suitable baths to deposit new colours on the bleached portions of the fabric. If the fabric is impregnated with aniline hydrochloride, aniline black is deposited at the same time that the original colour is removed.

The oxidation of colouring matters during the process of dyeing may be prevented by placing in the bath the negative electrode of a battery or small dynamo-machine, whilst the positive electrode is placed in a *small* vessel which communicates with the larger vessel through a diaphragm of parchment paper or earthenware, or by means of a bent tube. The hydrogen liberated at the negative pole prevents oxidation. To deposit heavy or noble metals on fabrics, the latter are impregnated with a thickened solution of the metallic salt and placed in contact with the negative electrode, when the metal is precipitated in the fibres.

The hydrogen liberated at the negative electrode may be used in the preparation of indigo vats, &c., instead of the usual reducing agents. Oxidation may be prevented by means of a feeble continuous current.

C. H. B.

**Cause of the Acid Reaction Exhibited by some Kinds of Paper.** By FEICHTINGER (*Dingl. polyt. J.*, 245, 174—176).—The author had occasion to examine a variety of writing and printing paper, with the view of detecting the presence of woody admixtures and mineral filling substances, &c. He found that all papers which had been treated with size made from resin, had an acid reaction, whilst papers treated with animal size did not exhibit any acid properties. To ascertain the cause of this, a large number of papers was investigated, and it was found that the acidity was caused by the presence of free sulphuric acid. The author concludes that this is due either to the formation of free sulphuric acid on treating the paper with sodium thiosulphate, after bleaching it with chlorine, and imperfect washing; or to the use of alum or aluminium sulphate in the sizing operation, the vegetable fibre decomposing the aluminium salt by superficial attraction, as in the case of dyeing, so that a basic salt is precipitated by the vegetable fibre with the simultaneous formation of free acid. Although unable to prove definitely, without further investigation, whether the acid reaction is attributable to the first or second cause, the author, finding that paper does not exhibit this property when treated with animal size, considers that it depends on the addition of alum to paper sized with resin.

D. B.

**Yolk of Egg.** By P. CARLES (*J. Pharm. Chim.* [5], 6, 26—28).—To prevent the shrivelling and drying of the yolk of eggs, so largely used by curriers, it is by some moistened with water, by others mixed with salt, this, however, coagulates it; whilst sometimes alum or alkaline sulphates are added to hinder decomposition, to which, as well as the loss of water, the drying up is due: but these substances, although not injurious to the leather, dilute the yolk, technically known as *mucilage*, and lessen the percentage of egg oil, which is the valuable constituent.

To test the purity of the *mucilage*, it has been proposed to rely on the sp. gr., that of fresh yolk being taken at 1.025, but the substances used for its preservation would materially affect the results. Since the egg oil is the important constituent, the author proposes to estimate this by first drying the yolk at 100°, and determining the water, then washing the weighed residue with ether, to remove the oil, evaporating the solution and weighing the residue. The insoluble residue is weighed and ignited, which gives the ash and organic matter insoluble in ether.

L. T. O'S.

**Adulteration of Balsam of Peru.** By O. SCHLICKUM (*Arch. Pharm.* [3], 20, 498—517).—The author has examined the means for detecting and estimating the following adulterants:—Castor-oil, balsam of copaiva, purified storax, alcoholic solutions (of a balsamic consistence) of benzoin and of colophony.

The sp. gr. is of great importance. The sp. gr. of genuine balsam of Peru being 1.140—1.150, and that of all the above adulterants being less.

Trials with various solvents showed that alcohol was of no use. Carbon bisulphide, however, gave better results. Treating 1 part of the bodies under consideration with 2 parts of carbon bisulphide, balsam of Peru gave 16 per cent. of resinous residue; storax, solution of colophony, balsam of copaiva, and castor-oil, dissolved completely; and benzoin gave a 60 per cent. residue.

On treating 1 gram of the above substance with 0.3—0.4 gram dry calcium hydroxide, and treating with water on the steam-bath for three or four hours, benzene extracted from the residue: from balsam of Peru 41 per cent., from purified storax 35 per cent., from balsam of copaiva, its essential oil, and scarcely anything from castor-oil, or solution of benzoin or colophony.

On shaking an ethereal solution of balsam of Peru with aqueous ammonia (0.96 sp. gr.), two yellowish-brown layers are obtained, with brownish flocks floating between them. The upper layer is an ethereal solution of the balsam, and gives, on evaporation, as residue, about 80 per cent. of the original balsam. On acidifying the lower ammoniacal layer with acetic acid, it becomes milky, the turbidity disappears when it is boiled, but on cooling, it again becomes turbid from separation of cinnamic acid. The benzoin solution behaves in a similar manner. Castor-oil is so completely dissolved by the upper layer, that scarcely anything separates on acidifying the lower. The resin in solution of colophony and balsam of copaiva combines with the ammonia, so that on acidifying and boiling much solid resin separates. With purified storax, no separation of the fluid into two layers takes place, but a stiff glue is formed, which will scarcely flow from the glass.

On treatment of 1 gram of the substances with 1 gram of sulphuric acid, and subsequent washing, first with hot and then with cold water, a solid brittle mass is formed (except with castor-oil), which in the case of balsam of Peru, balsam of copaiva, and colophony, is completely, and with storax and benzoin only partly, soluble in ether. In the case of castor-oil a greasy mass, perfectly soluble in ether, is produced. The residue in the case of the benzoin is completely soluble in alcohol or acetone, but the resin from storax leaves a residue (about 7 per cent. of the original storax), called styrogenin by E. Mylius, who found its composition to be  $C_{26}H_{40}O_3$ . This body was first observed by the author (*Pharm. Zeit.*, 1881).

The above properties of the different adulterants are utilised by the author for their detection and quantitative estimation.

F. L. T.

**A New Use for Potatoes.** By G. BOECK (*Bied. Centr.*, 1882, 575).—If potatoes be peeled and treated with 8 parts sulphuric acid and 100 parts water, then dried and pressed, a mass is obtained resembling celluloid, which can be used instead of meerscham or ivory.

E. W. P.



# ERRATA IN VOL. XLII.

Page.	Line.		
79	12 from bottom	<i>for</i> 8 per cent.	<i>read</i> 0·08 per cent.
217	12	„ „ chlorestrophan	„ „ cholestrophan.
489	28 from top	„ $C_8H_{18}O_3$	„ $C_8H_{16}O_3$ .
499	4 from bottom	„ $C_{10}H_{16}O$	„ $C_{10}H_{16}O_4$ .
552	12	„ „ 24, 2	„ 24, 406—423.
552	21	„ „ Neuhaven	„ Neubauer.
556	6	„ „ 4, 329	„ 5, 10—13.
697	30 from top	„ Divers	„ Davis.
729	21	„ „ potassium	„ potash.
729	14 from bottom	„ an alkaline solution, and shows	„ in alkaline solution shows.
815	9 from top	„ $\begin{matrix} FeO \\ (as\ silicate) \\ 8\cdot64 \end{matrix}$	„ $\begin{matrix} FeO \\ (as\ silicate) \\ 8\cdot84. \end{matrix}$
938	25	„ „ $C_5H_2Cl_4Br.O_3$	„ $C_5H_2Cl_4Br_2O_3$ .
944	10	„ „ $(CCl_2Br.COO_2)_2$	„ $CCl_2Br.COO$ .
944	23	„ „ + $H_2O$	„ + $2H_2O$ .
946	21	„ „ <i>Ber.</i> , 617—618	„ <i>Ber.</i> , 15, 617—618.
947	6	„ „ $.C <$	„ $.CH <$ .
954	1	„ „ 100—120°	„ 120—130°.
1179	15	„ „ 0·0220	„ 0·9220.
1185	1	„ „ $O_4$	„ $O_2$ .
1295	7 from bottom	„ $\gamma$ -mononitroisophthalic acid	„ $\gamma$ -monamidoisophthalic acid.